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Chlorination of Aquatic Humic Substances

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CHLORINATION OF AQUATIC HUMIC SUBSTANCES

by

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16. ABSTRACT

This research program was initiated with the overall objective of increasing our understanding of the chemical structures of aquatic humic material and their behavior during chemical oxidation in particular with chlorine.

Experimental methods were devised for the isolation of humic and fulvic acid fractions from natural surface waters. These methods involve the classical precipitation of humic acids from large volumes of raw water followed by concentration through settling and centrifugation. Fulvic acid materials were concentrated by adsorption on macroreticular XAD-2 resin followed by base elution. Experimental conditions were devised for the controlled oxidation of these samples with $KMnO_4$ and with aqueous chlorine solutions followed by solvent extraction, formation of methyl esters and GC/MS analysis. The criteria for identification of degradation products employing low resolution EI, high resolution EI, and CI mass spectrometry are included in appended material. Chlorination experiments were also conducted on selected model compounds as dictated by the results of the whole sample degradation experiments.

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

Byproducts of the reactions between drinking water disinfectants and naturally occurring organic materials in the source water are now being recognized as a potential health problem. This report describes research conducted to elucidate dominant chemical structures of aquatic humic material and to determine how these materials react with aqueous chlorine to form various byproducts identified. The work was sponsored by the Drinking Water Research Division of the E.P.A. Municipal Environmental Research Laboratory as part of a larger effort to assess the water treatment implications of these byproducts.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

ABSTRACT

This research program was initiated with the overall objective of increasing our understanding of the chemical structures of aquatic humic material and their behavior during chemical oxidation in particular with chlorine.

Experimental methods were devised for the isolation of humic and fulvic acid fractions from natural surface waters. These methods involve the classical precipitation of humic acids from large volumes of raw water followed by concentration through settling and centrifugation. Fulvic acid materials were concentrated by absorption on macroreticular XAD-2 resin followed by base elution. Experimental conditions were devised for the controlled oxidation of these samples with $KMnO_4$ and with aqueous chlorine solutions followed by solvent extraction, formation of methyl esters and GC/MS analysis. The criteria for identification of degradation products employing low resolution EI, high resolution EI, and CI mass spectrometry are included in appended material. Chlorination experiments were also conducted on selected model compounds as dictated by the results of the whole sample degradation experiments.

The results of the $KMnO_4$ oxidation experiments established that the principal identifiable degradation products of aquatic humic acid are aromatic polybasic acids, some of which are hydroxylated. The degradation mixture also contains a complex misture of aliphatic mono- and dibasic acids in lesser concentrations. Although the overall yields of these experiments were low (20-30 wt.%) a very large proportion of the chromatographable products were identified through GC/MS. Since dihydroxy aromatic configurations were shown to be significant contributors to the humic macromolecular structure, the reaction of resorcinol as a model compound with HOCl was investigated carefully. A cyclic chlorinated diketone intermediate was identified along with other non-$CHCl_3$ reaction products. In addition to chloroform a large number of chlorinated and unchlorinated acids, phenols, and ketones were produced. Ring cleavage products such as saturated and unsaturated, chlorinated and unchlorinated aliphatic mono- and dicarboxylic acids were major products of model as well as natural humic materials. The yields of these reactions (8-17 wt.% of TOC) were slightly lower than the permanganate yields. The majority of the identified chlorine degradation products were unchlorinated aliphatic and aromatic acids. No chlorinated aromatic compounds were identified.

Aquatic humic acids are thus shown to be important precursors of not only chloroform but also a larger number of other chlorinated and unchlorinated organic compounds. Chlorine at high pH was a strong oxidizing agent for aquatic humic materials. Although the results of this study have yielded significant chemical structural information on aquatic humic material, the findings are insufficient for the construction of a reliable model of aquatic humic acid structures.

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The authors are deeply appreciative for the guidance and support of Alan A. Stevens, U.S. EPA, who served as our Project Officer.

SECTION 1

INTRODUCTION

Aquatic humic material has been heavily implicated as an important reaction precursor of trihalomethanes in natural water systems exposed to chlorine. It has been assumed that humic materials are ubiquitously present in natural waters and have sufficient chemical similarity in time and space to account for the observed property of producing $CHCl_3$ when exposed to chlorine. Further it has been assumed that the mechanism of the Cl_2/humic interaction involves the classical haloform reaction, and that trihalomethanes are the principal reaction product. Public and governmental concern over the presence of $CHCl_3$ in drinking water has focused attention in this phenomena and the aforementioned assumptions have been made due to inadequacies in our scientific understanding of the fundamental chemical structures present in aquatic humic materials and therefore the reactions of these structures with chlorine.

The research described herein has focused on the characterization of the chemical reactions of aquatic humic material with hypochlorous acid. First a comprehensive literature review was conducted and is presented in Section 3. The experimental approach has involved a) the chemical degradation of natural aquatic humic material to gain insight into the dominant chemical structures present in this natural product material, b) the reaction of HOCl with model compounds having structures similar to the degradation products and c) identification of non-volatile chlorinated and non-chlorinated degradation products of natural aquatic humics with HOCl.

Each experimental direction is described separately in the sections which follow, although it should be noted that the experimental planning of each section was heavily influenced by the results of current work in other sections. For instance, early model compound work established that total trihalomethanes were a minor portion of the total chlorine demand and subsequently only less volatile reaction products were emphasized in the actual humic chlorination experiments. Similarly the dominance of aromatic products in the oxidative degradation mixtures resulted in the exclusion of aliphatic compounds in the model compound experiments.

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SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The oxidative degradation experiments reported here have generated significantly more chemical structural information on aquatic humic material than was previously available in the literature. Controlled oxidation with $KMnO_4$ followed by solvent extraction, formation of methyl esters and GC/MS analysis has established that the principal identified degradation products of aquatic humic acid are aromatic polybasic acids, some of which are hydroxylated. The degradation mixture also contains a complex mixture of aliphatic mono- and dibasic acids in lesser concentrations. Although most of the chromatographable degradation products were tentatively identified (low resolution EI, high resolution EI, CI mass spectrometry), only 20-30 wt.% of the original humic carbon is accounted for by the identified products. The chemical data generated in this study do not provide a fully adequate scientific basis for modeling humic structures. However, a hypothetical structure is presented which would account for the observed data.

Chlorination of both aquatic humic materials directly, as well as model compounds shown to be major component parts of the aquatic humic and fulvic materials, produced chloroform. Dihydroxy aromatic configurations were shown to be significant contributors to the humic macromolecular structure and therefore the reaction of resorcinol with HOCl was investigated carefully as a model. A cyclic chlorinated diketone intermediate was identified along with other non-$CHCl_3$ reaction products. In addition to chloroform a large number of chlorinated and unchlorinated acids, phenols and ketones were produced. Ring cleavage products such as saturated and unsaturated aliphatic mono- and dicarboxylic acids were major products of model as well as natural humic materials. Only small portions(8-17 wt.% of TOC) of the aquatic humic material subjected to high pH and excess chlorine yielded products identifiable by gas chromatography and mass spectrometry. Thus, OCl^- is a significant degrader of the humic macromolecule but it is not as effective as alkaline $KMnO_4$. The majority of the identified chlorine degradation products were unchlorinated aliphatic and aromatic acids. The aromatic acids are primarily polycarboxylic suggesting carbon substituted on the aromatic rings at 3 or more sites in the undegraded macromolecule, in agreement with the $KMnO_4$ data. No chlorinated aromatic compounds were identified, however.

Aquatic humic materials are thus shown to be important precursors of not only chloroform but also a large number of other chlorinated and unchlorinated organic compounds. Although aromatic compounds dominate both the $KMnO_4$, and HOCl degradation products they do not appear to chlorinate directly. The experimental procedures employed in this study have shown significant promise as a tool for increasing scientific understanding of fundamental aquatic

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humic chemistry. More structural information can be gained from these methods through additional research on increased oxidative yield and extraction and separation efficiencies. A method for following the changes in macromolecular size/polarity during the degradation would be extremely useful.

The development of the techniques reported here permits an even wider range of useful experimentation. Questions in need of evaluation include; do fulvic acids (most of the TOC) yield qualitatively and quantitatively similar results; do the chemical properties of the humic and fulvic fractions vary seasonal for any source; what chemical variability exists between natural water sources. In addition, the effect of oxidant/disinfectants other than OCl^- on humic structures should be evaluated.

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SECTION 3

LITERATURE REVIEW

INTRODUCTION

In 1974 J. J. Rook (1) hypothesized that water-borne humic materials in the Rotterdam water supply were chemical precursors of several trihalogenated methane species detected in the Berenplaat treatment plant effluent. At the same time interest in the USA in possible adverse human health effects of trihalomethanes was growing (2) as a result of reports (3-7) that $CHCl_3$ and other halogenated organic compounds were present in New Orleans drinking water and that the consumption of this water was correlated with the incidence of cancer in white males (8). Although the adequacy of the statistical methods employed and the validity of the human health interpretations drawn in this study were challenged (9), other scientific investigations (10,11) established that the chlorination process as commonly practiced can result in the formation of a variety of chlorinated organic compounds, many of which are known or suspected carcinogens.

As concern mounted over the safety of publicly supplied drinking water, Congress passed the Safe Drinking Water Act which was signed into law (PL93-523) by the President in December of 1974. Section 1442 of this act required that the Administrator of EPA conduct a comprehensive study of public water supplies and drinking water sources to determine the nature and extent of contamination by carcinogenic substances. Initial results of this survey (12) indicated that four trihalomethanes, $CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$ are widespread in chlorinated drinking waters in the USA and result from the chlorination process. Additional EPA research (13) and further work by Rook (14,15) established that the observed concentrations of trihalomethanes can be formed by chlorinating aqueous solutions of natural humic material, commercial humic material, or model phenols and cyclic ketones and that trihalomethane production is primarily influenced by the nature and concentration of the organic substrate, the nature of the aqueous chlorine compound, pH, temperature and the Cl_2/C ratio.

The close relationship of aquatic humic material to soil organic matter and to lignitic and extractive material in woody tissue had been established by earlier investigators (16-18). Although Rook's most recent articles emphasize the role of m-dihydroxy aromatic configurations, the chemical nature of aquatic humic substances is not sufficiently established to say with certainty that these structures are the most important participants in the halomethane production reactions and because of the obvious relevance of research findings in the areas of lignin and humic acid chemistry, an effort was made to summarize the relevant research in each of these areas. The

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reviews of lignin and humic acid chemistry are not intended to be exhaustive, rather they will rely upon other reviews where possible and will attempt to describe the most important research findings relevant to the chemical structure and reactivity of these natural product materials.

LIGNIN CHEMISTRY

Woody tissue is the predominant form of organic carbon on the earth's surface (19) and its major chemical components are described in Table 1. In mature wood the amount of lignin varies between 18 and 38% (wt./wt.) with widely varying amounts present also in grasses and ferns. This review will concentrate on the lignin and extractive components since these materials are the only components with appreciable stability in the environment and which contain aromatic and polyphenolic material.

TABLE 1. COMPONENTS OF WOODY TISSUE (16)

A. Major Cell Wall Components

  1. Lignin
  2. Polysaccharides

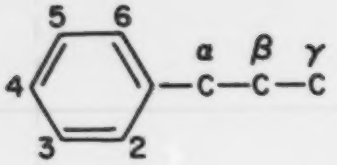
     a. Cellulose; hydrolysis yields D-glucose
     b. Noncellulose polysaccharides; hydrolysis yields various monomeric units

B. Extraneous Components

  1. Components soluble in neutral solvents or volatile with steam, such as extractives, fats and resins
  2. Components largely insoluble, such as inorganic, pectic and proteinaceous substances

Lignin differs from other natural polymers such as carbohydrates and proteins in that lignin is predominantly aromatic. It is also relatively insoluble in known solvents, not hydrolyzable to monomeric units and is devoid of the highly regular structure characteristic of other classes of natural polymers. These properties have made structural studies on lignin difficult and several excellent reviews (20,21,22) have emphasized that a fully adequate chemical definition of lignin has not been developed.

By the late 1940's lignin chemists had established that the elemental composition and other chemical and physical properties of spruce lignin conformed closely to that of a guaiacylpropane polymer (20). Extensive degradative research on whole lignin preparations supports the concept that the phenylpropane unit is the basic building block in the macromolecule. Various phenylpropanoid derivatives have been identified in both oxidative and reductive degradation mixtures (Figure 1 and Table 2). Yield data show that lignin is not completely degradable to monomers primarily because of C-C intermonomeric linkages which are resistant to these degradative techniques.



PHENYLPROPANE UNIT

On the basis of these research results softwood lignins (gymnosperm) are

TABLE 2. YIELDS OF PHENYLPROPANE DERIVATIVES FROM LIGNIN (20)

Lignin	Method	Derivative Isolated	Estimated Yield (% Lignin)
Aspen	Hydrogenation	I, II, III	44
Maple	Hydrogenation	I, II, III	25
Maple	Hydrogenation*	IV, V, VI	10-15
Spruce	Na in liquid NH_3	VII, VIII	28
Spruce	Ethanolysis	IX, X, XI, XII	10
Maple	Ethanolysis	IX to XV	20

---

*with Raney nickel catalyst

considered to represent polymers containing guaiacylpropane units exclusively, whereas hardwood lignins (angiosperm) apparently contain both guaiacyl and syringylpropane units. Plant lignins also contain p-hydroxylphenylpropane units (20,21,22).

Phenylpropane units are linked together in the lignin macromolecule by both ether and carbon to carbon linkages. Ether linkages are more susceptible to chemical degradation and may involve a) the α carbon on one alkyl side chain with either an α or β carbon on another side chain (α-alkyl type) or b) the β carbon on one side chain with the hydroxylated aromatic ring carbon of another phenylpropane unit (β-4' type). Carbon to carbon linkages may involve both side chains (α-α', β-β'), both aromatic rings (5-5') or the alkyl side chain and the aromatic ring (β-5'). The side chain carbon atoms may be in various states of oxygenation or unsaturation, and may contain methyl ketone, allyl or secondary alcohol configurations, in addition to those shown in Figure 1.

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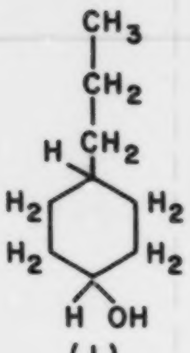

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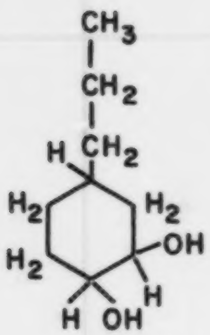

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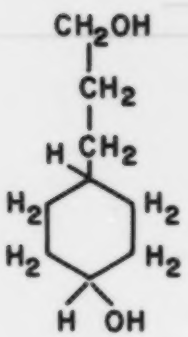

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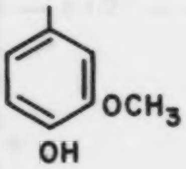
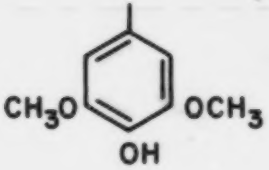


Guaiacyl



Syringyl

Guaiacyl-CH_2-CH_2-CH_2 OH
(IV)

Syringyl-CH_2-CH_2-CH_2OH
(V)

Syringyl-CH_2-CH_2-CH_3
(VI)

Guaiacyl-CH_2-CH_2-CH_3
(VII)

Guaiacyl-CH_2-CHOH-CH_3
(VIII)

Guaiacyl-COCH(OC_2H_5)-CH_3
(IX)

Guaiacyl-CH(OC_2H_5)-$COCH_3$
(X)

Guaiacyl-$COCOCH_3$
(XI)

Guaiacyl-CH_2 -$COCH_3$
(XII)

Syringyl-COCH-(OC_2H_5)-CH_3
(XIII)

Syringyl-$COCOCH_3$
(XIV)

Syringyl-CH_2-$COCH_3$
(XV)

Figure 1. Phenylpropane degradation products from lignin (20).

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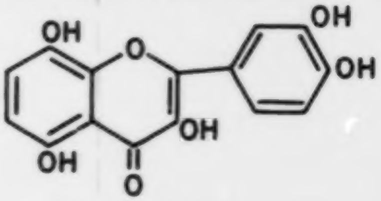
Ether linkages in lignin are generally broken by alkaline hydrolysis although high temperatures (150-200°C) are required. Exposure to alkaline nitrobenzene at elevated temperatures results in cleavage of the propane side chain to a one carbon aldehyde group. Stronger oxidations ($KMnO_4$) result in one carbon acid groups on the α side chain carbon and rupture of β-β' interaromatic linkages (20,21).

In general, the alkaline nitrobenzene procedures result in significant yields (20) with as much as 32% of the phenylpropane units isolated in the form of identified products in the case of softwoods and as much as 50% for hardwoods. Vanillin is the principal component in such degradation mixtures and by comparison of vanillin yields of nitrobenzene oxidation of lignins to that obtained from model compound oxidations lignin chemists estimate that ether type linkages constitute approximately 50% of the intermonomeric linkages in the original macromolecule.

The extractive fraction of woody tissue also constitutes a significant source of natural polyphenols. Kurth and Hubbard (23) showed that the yellow coloring matter in ponderosa pine bark is 3.3', 4,4', 5,8-pentahydroxy flavone (XVI). Hergert (24) found that isomers of leucocyanidin (XVII) were present in aqueous bark extracts of twelve species of conifers and that most conifers contain a variety of additional phenolic and polyphenolic substances including phloroglucinol (XVIII), quercetin (XIX), coniferaldehyde (XX) and gallic acid (XXI). Other workers (25) have isolated pyrolysates of natural phlobaphene and tannin material from whole wood and identified catechol, guaiacol, 1,2-dimethoxy benzene and phenol with their *para*-methyl-, ethyl-, and n-propyl homologues. The extractive fraction of woody tissue may also contain some of the guaiacyl and syringyl moieties described earlier (148).

(XVI)



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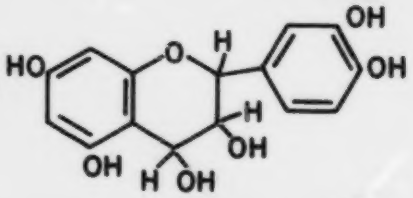

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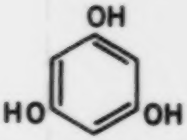

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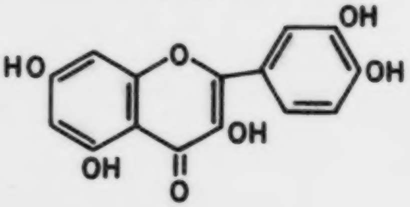

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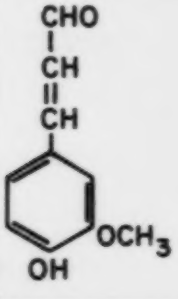

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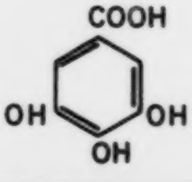

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SOIL HUMIC MATTER

Early Studies

Achard (26) in 1786 was the first to isolate humic matter from the total soil matrix. According to Packham (27), later work was provided by Sprengel (28) who gave the first detailed description of humic matter of soil. Much of the early work correctly recognized that what had been collectively called humic matter in soil could be further separated and classified. As reported by Schnitzer (29), Berzelius and others between 1830 and 1860 made the first attempts at such classifications. Finally in 1919 Oden (30) described the classification system in common use today. Later work as summarized by Burges (31) included the efforts of Shmuk (32) (1924), Waksman (33) (1963), and Tinsley and Maung (34)(1956) who attempted to define the chemical-physical properties and structure of humic acid. For an indepth outline of the early history of soil humic matter reviews by Waksman (33), Tyurin (35), Bremner (36,37), and Knonova (38) are available.

Soil Fractionation and Classification

According to Black and Christman (39) prior to the 1919 classification system of Oden there were 43 different names for the 4 fractions that could be separated from soil humics. Oden's system thus provided considerable order and came into widespread use, which continues to date. Table 3 describes Oden's classification system. Oden's system, however, is not the only one used today. Many other fractionation/classification schemes have been described by Schnitzer (29).

Stevenson and Butler (40) further subdivided humic acid into "brown H. A." (soluble) and "gray H. A." (insoluble) by treating humic acid with base and electrolyte. Salfeld (41) used tetrahydrofuran for fractionating humic acid, and Martin et al. (42) used the same compound for fractionating fulvic acid. Theng et al. (43) fractionated a soil humic acid by "salting-out" with

TABLE 3. ODEN'S CLASSIFICATION OF HUMIC SUBSTANCES (27)

Group Name	Alternative Names	Definition
Humus Coal	Humin, Ulmin	Insoluble in sodium hydroxide.
Fulvic Acid	Crenic and Apocrenic Acids	Soluble in sodium hydroxide and mineral acid.
Hymatomelanic Acid	Haematomelanic, Hematomelanic, or Ulmic acid	Soluble in sodium hydroxide. Insoluble in mineral acid. Soluble in alcohol.
Humic Acid		Soluble in sodium hydroxide. Insoluble in mineral acid and alcohol.

ammonium sulfate. Linqvist (44) effected fractionation of soil humic matter by varying ionic strength and pH. Sowden and Devel (45) fractionated a soil fulvic acid by adding varying amounts of Pb^{2+}, Ba^{2+}, and Cu^{2+}; and Kahn (46) among others used Sephadex columns to fractionate humics from various soils. Dragunov and Murzakov (47) fractionated a soil-fulvic acid into thirteen chemically and spectroscopically different fractions using adsorption column chromatography, while Veselinka et al. (48) used zonal paper electrophoresis for fractionation of soil humic acid. Leenheer and Malcolm (49) were able to fractionate both humic acid and fulvic acid from soils by a continuous zone electrophoresis technique.

It is thus quite apparent that the common definitions of humic acid, fulvic acid, etc. are strictly *operative* and depend intimately on which classification scheme they originate from. Further, some fractions of a given classification scheme may be artifacts of the particular system. This view, as reported by Schnitzer (29), is held by Stevenson and Butler (40) with regard to hymatomelanic acid from Oden's system. In several cases components such as F. A. and H. A. previously thought to be discrete and indivisible were further fractionated. Apparently none of the fractionation/classification systems can be regarded as *absolute*.

Chemical Characterization of Soil Humics

Schnitzer (29) summarizes the results of elemental analyses performed on six soil humic acids, three soil fulvic acids and two soil humins. These results, presented in Table 4, show that humic acids contain more C and N but less oxygen than fulvic acids. Humins, on the other hand, appear similar to humic acids from the standpoint of elemental analysis. Nitrogen distribution in soil humics has been reviewed by Bremner (50,51), and Schnitzer (29) also discusses the subject indicating that the nitrogen in soil humic acid, fulvic acid and humin can be present as amino acids, amino sugars, and ammonia nitrogen. Table 5 illustrates percentages of these substances.

It is important to note from this tabulation that almost half of the nitrogen in either case is unaccounted for. Schnitzer offers the opinion that this nitrogen is either adsorbed onto or actually chemically bonded to the humic material. This is a point of contention with some workers. As reported by Burges (31), Tyurin (35) is of the opinion that nitrogen in humic acid is present as an unavoidable consequence of protein being mixed with humic material. Burges (31) shares this opinion and offers experimental evidence to support this claim. Later work by Sowden and Schnitzer (52) accounted for only approximately 50% of the soil nitrogen. These workers ascribed the discrepancy to adsorption and/or precipitation on the resin used to purify the humic material. Schnitzer (29) summarizes an important point observed by Bremner (55,56) that the nature of the solutions used to extract the humic acid and fulvic acid from soils have a marked effect on the resultant content and distribution of nitrogen. An extensive amount of work has been done on the distribution of roughly twenty amino acids in soil humic acids and fulvic acids. The works of Kahn and Sowden (53,54) and Sowden and Schnitzer (52) provide tabular summaries with percent of each amino acid found. The nitrogen question must be regarded as presently unresolved.

TABLE 4. PERCENT ELEMENTAL COMPOSITION OF SOIL HUMIC ACIDS AND SOIL FULVIC ACIDS (29)

C	H	N	S	O
		SOIL HA's		
56.4	5.5	4.1	1.1	32.9
53.8	5.8	3.2	0.4	36.8
56.7	5.2	2.3	0.4	35.4
56.4	5.8	1.6	0.6	35.6
60.4	3.7	1.9	0.4	33.6
60.2	4.3	3.6	a	31.9
		SOIL FA's		
42.5	5.9	2.8	1.7	47.1
47.6	4.1	0.9	0.1	47.3
50.9	3.3	0.7	0.3	44.8
		SOIL HUMINS		
55.4	5.5	4.6	0.7	33.8
56.3	6.0	5.1	0.8	31.8

a: Not determined

TABLE 5. NITROGEN DISTRIBUTION IN A HUMIC ACID, A FULVIC ACID, AND A HUMIN(29)

Type of Material	Nitrogen Content (%)	% Amino Acid N	% Amino Sugar N	% Ammonia N	% Nitrogen Accounted For
Humic Acid	4.07	28.3	1.3	19.8	49.4
Fulvic Acid	3.87	26.4	3.6	15.1	45.1
Humin	4.60	36.1	1.6	22.1	59.8

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Schnitzer (29) has summarized studies of the distribution of oxygen-containing functional groups in soil humic acids and fulvic acids by a series of workers (57-62). Table 6 summarizes the concentrations of oxygen containing functional groups and total acidity for five soil humic acids and three soil fulvic acids. A marked difference exists between fulvic acid and humic acid; the latter containing less total and carboxyl acidity primarily.

The occurrence of quinones in soil humics has been suggested by several researchers (38,63,64). According to Schnitzer (29) research in the area has been hampered by the lack of reliable methods for the determination of quinones. Schnitzer is also of the opinion that if quinone groups exist in humic materials they occur not as simple compounds but rather in complex structures.

TABLE 6. OXYGEN-CONTAINING FUNCTIONAL GROUPS AND TOTAL ACIDITY IN SOIL HUMICS (29)

Total Acidity	Carboxyl	Phenolic OH	Alcoholic OH	Carbonyl	Methoxyl
			SOIL HA's		
6.6	4.5	2.1	2.8	4.4	0.3
8.7	3.0	5.7	3.5	1.8	a
5.7	1.5	4.2	2.8	0.9	a
10.2	4.7	5.5	0.2	5.2	a
8.2	4.7	3.6	a	3.1	0.3
			SOIL FA's		
14.2	8.5	5.7	3.4	1.7	a
12.4	9.1	3.3	3.6	3.1	0.5
11.8	9.1	2.7	4.9	1.1	0.3

---

a: Not determined

Physical Characterization of Soil Humics

Spectroscopic studies with soil humics have been extensively reviewed by Schnitzer (29). Regions of the electromagnetic spectrum used by various workers include NMR (65), ESR (66-69), IR (70-72), visible (38,73), UV (72, 74), and X-ray (75,76). The infra-red methods have been used for characteri-

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zation of soil humics of different origins and for detection of both unwanted changes brought about by various chemical extractions and desired chemical changes affected by reactive techniques such as methylation, esterification, and acylation. NMR methods have been used to obtain limited structural information. Visible methods yield information for characterization of humic acids and fulvic acids from different types of soils (viz: Podzols *vs* Krasnozems *vs* Chernozems, etc.). ESR work has centered around identification of paramagnetic organics (e.g., quinones) thought to exist in humic materials in large amounts. X-ray methods have concentrated on X-ray diffraction (i.e., no use of XRF, ESCA, Auger, etc. were found by the reviewers) for the purpose of gaining insight into structural characteristics. UV methods have in general provided little information with the exception of the use of the UV and visible portions of the spectrum in fluoresence studies. These methods have been used to follow fractionation procedures and chemical changes brought by pH changes.

Potentiometric titrimetry methods were used by Schnitzer and Desjardins (59) to determine equivalent weights of soil fulvic and humic acids. These results indicated an equivalent wt. of 76 for fulvic acid and 165 for humic acid. Other electrochemical titrimetry methods have been reviewed by Schnitzer (29).

Schnitzer (29) has reviewed the efforts to determine molecular weight of soil fulvic and humic acids by a number of researchers (59,77-80). Methods used include vapor pressure osmometry, freezing point depression, gel filtration, diffusion, sedimentation, isothermal distillation, and viscometry.

Schnitzer points out that several definitions of molecular weights are in use - each depending in particular on which method is used. So-called number average molecular weight, $\overline{Mn}$; weight average molecular weight, $\overline{Mw}$; and z-average molecular weight, Mz, are all seen in the literature. According to Schnitzer for a homogeneous substance $\overline{Mn} = \overline{Mw} = \overline{Mz}$. However, for heterogeneous systems such as soil humic and fulvic acids it is often true that $\overline{Mn} < \overline{Mw} < \overline{Mz}$.

The results of various molecular weight determinations are summarized in Table 7. There is a great deal of variability in the reported results which is apparently due to the different methods used. Schnitzer and Skinner (81), in fact, found that the molecular weights measured by means of Sephadex gels (gel filtration) could be 2 to 10 times higher than the types of molecular weights determined by vapor pressure osmometry or freezing point depression.

Other physical characterization methods that have been reviewed by Schnitzer (29) include electron microscopy, thermal analysis, viscosity studies, and a radiocarbon dating. In the opinion of the present reviewers these represent ancillary techniques in the present state-of-the-art applications to soil humics.

Structural Characterization of Soil Humics

Schnitzer (29) has extensively reviewed the degradative methods applied to soil humics and has divided them into three major classes: oxidative,

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reductive and biological. In his opinion the oxidative methods have been more fruitful because humic materials contain so much oxygen that they are difficult to reduce. Minor classes also discussed include hydrolysis with water, acid hydrolysis, and basic hydrolysis; although these do not provide significant information as humic materials appear to be resistant to hydrolytic degradation.

TABLE 7. REPORTED MOLECULAR WEIGHT DETERMINATIONS FOR SOIL HUMIC MATERIALS (29,59,81)

Method	Molecular Weight Definition	Value Reported
	Fulvic Acid	
Vapor Pressure Osmometry	$\overline{M}_n$	951
Freezing Point Depression	$\overline{M}_n$	669
Vapor Pressure Osmometry	$\overline{M}_n$	688
	Humic Acid	
Isothermal Distillation	$\overline{M}_n$	~1,000
Freezing Point Depression	$\overline{M}_n$	1,684
Diffusion	$\overline{M}_n$	4,500-26,000
Gel Filtration	$\overline{M}_w$	14,000-200,000
Sedimentation	$\overline{M}_z$	~53,000
Viscometry	$\overline{M}_w$	~36,000
Vapor Pressure Osmometry	$\overline{M}_n$	47,000-53,800

Oxidative Degradations--

Alkaline nitrobenzene oxidations have been applied to soil humics by Morrison (82) and by Wildung et al. (83). This method was important in isolating derivatives which established that lignin was a precursor of the undegraded humic material. In particular, significant amounts of syringyl, guaiacyl and p-hydroxyphenyl residues have been found as degradation products of this technique. Alkaline-CuO oxidation as described by Steelink et al.

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(84) and Green and Steelink (85) yields aromatic monomeric units with side chains: vanillin, *p*-hydroxybenzaldehyde, syringaldehyde, *p*-hydroxybenzoic acid, vanillic acid, 3,5-dihydroxybenzoic acid, and *m*-hydroxybenzoic acid. Noteworthy is the metadihydroxy species which indicates that lignin is not the sole precursor of soil humic material.

Alkaline permanganate oxidation as utilized by Hansen and Schnitzer (60) and further reviewed by Schnitzer (29) results in aliphatic carboxylic acids and benzene carboxylic acids. Schnitzer and Desjardins (86) employed alkaline permanganate oxidation and postulated that simple aromatic centers make up the parent soil humic material. Nitric acid oxidation of soil humic matter has been studied by Hansen and Schnitzer (87), who identified nitrophenols, nitrobenzoic acids, hydroxybenzoic acids and benzene carboxylic acids among degradation products. From these results they were able to postulate the existence of precursor "carbon skeletons" in the undegraded material. Schnitzer (29) discusses one further oxidative degradation technique that has received little attention in the study of soil humics: permanganate oxidation of methylated humic substances. The advantage of this technqiue is that prior methylation "protects" phenolic hydroxy groups against attack by permanganate during oxidation (see page 4). The results of some work with this technique on soil humics are presented by Schnitzer.

Reductive Degradations--

Zinc-dust distillation has been employed by Hansen & Schnitzer (88) in order to determine the presence of polycyclic rings in soil humic matter. Degradation products revealed by this technique included naphthalene, anthracene, phenanthrene, pyrene, and perylene. In Schnitzer's (29) review many other polyring compounds isolated by this technique are reported. Sodium amalgam reduction according to Schnitzer (29) has been used by a number of researchers (89-93). Compounds isolated included species suggesting a flavanoid contribution to the undegraded soil humic matter. Schnitzer (29) also discusses hydrogenation, a reductive technique that has been used by many workers with little success. The technique reportedly utilizes very high temperatures and pressures leading unavoidably to rearrangements and condensation reactions which limit the utility of the method.

Schnitzer (29) has concluded that biological degradation efforts are not fruitful because of the uncertainty as to which compounds are produced by the organisms and which actually originate from the soil humic material.

Schnitzer (29) also discusses an exhaustive methylation procedure which is reported (94) to be *non-destructive*. Schnitzer lists twenty classes of compounds obtained by the technique which had to date only been applied to soil fulvic acids. Based upon the results of the method. Schnitzer has proposed a structure for fulvic acid which consists of phenolic and benzene carboxylic acids joined by hydrogen bonding. His proposed structure is presented in Figure 2.

Davies et al. (95) discuss their preference of soil humic acid being a polyphenol-amino acid complex polymer. Murphy and Moore (96) discuss the drawbacks in an earlier model by Flaig (97). Figure 3 illustrates Flaig's

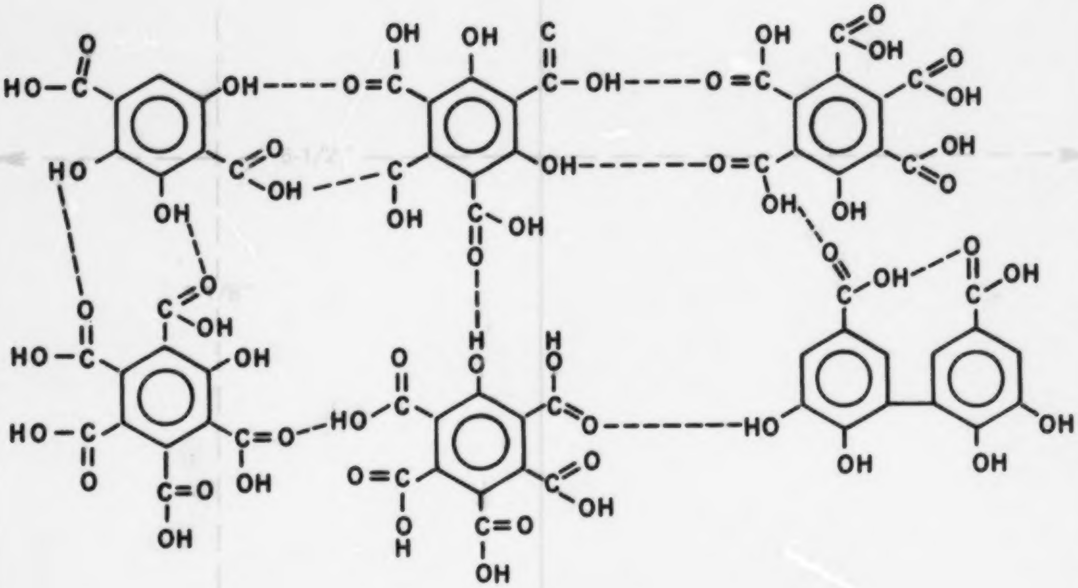

Figure 2. Soil fulvic acid structure proposed by Schnitzer (29).

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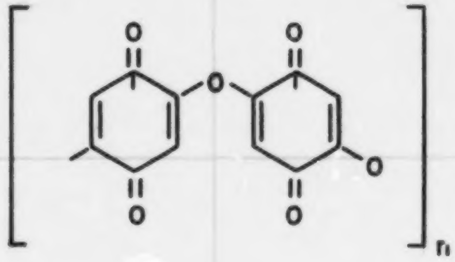
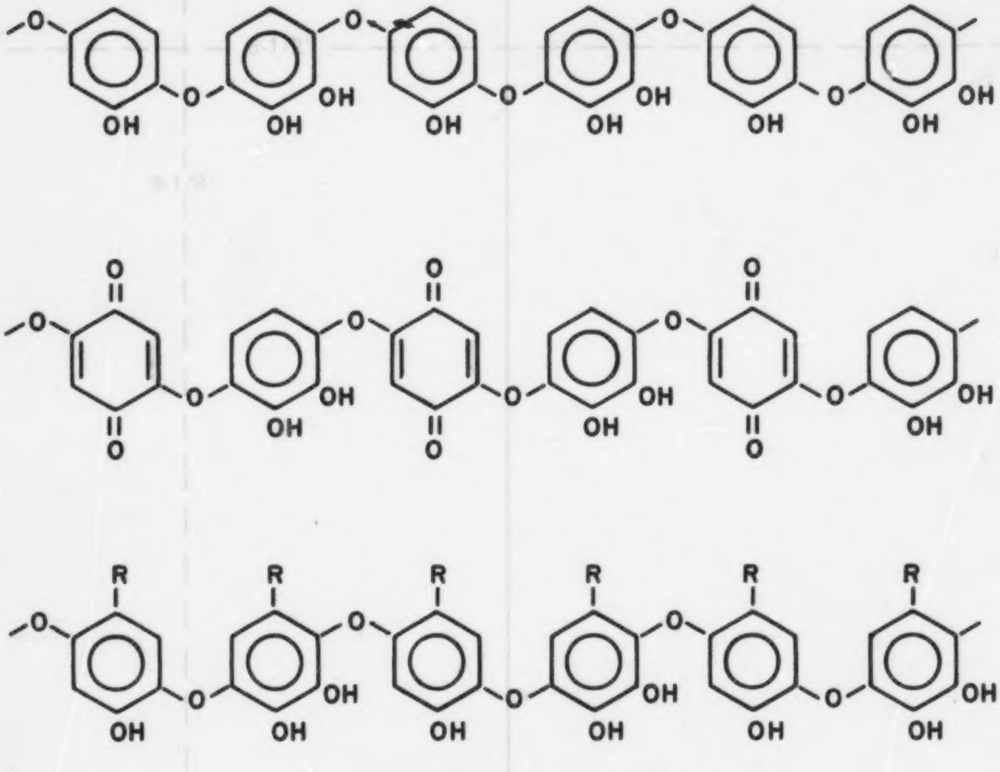


Flaig



$(R = C_1, C_2 \text{ or } C_3)$

Figure 3. Models of soil humic acid proposed by Flaig and Murphy and Moore (96).

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model and several models which they have proposed. They suggest that the amino acids may, in part, be attached to the polymeric molecules via esterification onto the hydroxyl groups.

Metal Binding Properties of Soil Humics

According to Schnitzer (29), Mortensen (98) ascribes the ability of soil humics to bind metals to the processes of ion exchange, surface-adsorption, chelation, coagulation and peptization. Theile et al. (99) studied the ion exchange characteristics of a humin and determined that the rate of exchange increased with the atomic weight for a particular series of metals studied: $Ca < Sr < Cd < Pb$. Beckwith (100) and others (101,102) as reported by Schnitzer (29), concluded that the metals of the first transition series complexed with soil humic material with stabilities following the Irving-Williams series: $Pb^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Cd^{2+} > Fe^{2+} > Mn^{2+} > Mg^{2+}$.

The capacity of soil humics to bind metals may in fact have very important purposes in nature. Schnitzer and Poapst (103) found that soil humics may, in fact, be the mechanism for the transport of iron, an essential nutrient, within plants. Schnitzer (29) reporting the findings of Szalay (104) indicates that the ability of humic materials to bind metals may lead to geochemical enrichments of 10^3-10^4: 1 for metals including U, Co, Ni, Fe, Zn, Cu, and La.

AQUATIC HUMIC MATTER

Early Studies

According to Packham (27), Berzelius was one of the earliest investigators in the field of aquatic humics; in 1806 he identified humic materials as being responsible for the light-yellow color of a spring water. Research continued with humic materials but emphasis apparently shifted mainly to soil humics until 1909. Then, according to Black and Christman (17), Aschan (105) carried out extensive research on the substances causing color in the waters of six Finnish rivers and lakes. For more information on previous research with aquatic humics, the reader is referred to the review by Black and Christman (17).

Separation Procedures

Black and Christman (18) reported the use of freeze concentration and vacuum evaporation methods to concentrate the humic materials in water. They subsequently used Oden's soil classification scheme to separate the concentrate into fulvic acid, hymatomelanic acid, and humic acid fractions. Shapiro (106) also used freeze concentration and vacuum evaporation methods but subsequently extracted the concentrated humics with ethyl acetate. Packham (27) reports that Datsko (107) extracted the humics directly with isobutanol. Lamar and Goerlitz (108) effected similar extractions with n-butanol. Christman and Ghassemi (16) used a macroporous anion exchange resin to separate aquatic humics from natural waters. The humic materials were subsequently eluted with a sodium chloride solution, extracted with n-butanol, vacuum evaporated, re-extracted with acetone, and finally dried under nitrogen. Packham discusses in some detail the use of ion exchange resins for separation of humic materials from water.

The results of separating 17 samples of aquatic humic matter into the classical fractions of Oden are summarized in Table 8. The first seven samples are from the work of Packham (27) and the last ten are from the work of Black and Christman (18). It is important to note that the preliminary separation procedure used by Packham (anion exchange) was different from that used by Black and Christman (freeze concentration or vacuum evaporation). Packham suggests that his technqiue may be less quantitative than that of Black and Christman.

TABLE 8. AQUATIC HUMIC MATTER SEPARATED INTO CLASSICAL FRACTIONS (18,27)

Sample No.	Fulvic Acid %	Hymatomelanic Acid %	Humic Acid %
1	83.0	13.1	3.9
2	85.4	10.2	4.4
3	86.0	10.2	3.8
4	65.5	18.3	16.2
5	76.5	18.5	5.0
6	80.9	13.9	5.2
7	57.8	32.2	10.0
8	87.0	11.2	1.8
9	87.5	11.6	0.9
10	87.7	10.3	2.0
11	89.6	9.6	0.8
12	88.8	11.1	0.1
13	87.9	11.3	0.8
14	85.0	14.3	0.7
15	89.5	8.4	2.1
16	86.4	12.9	0.7
17	82.8	16.6	0.6

As may be seen from examination of Table 8, the major component of aquatic humic matter is fulvic acid while the percentage of humic acid itself is relatively low. This is supported by Schnitzer and Desjardins (109) who examined the leachate of a humic Podzol and found 87% of the concentrated leachate to be fulvic acid. In another work Schitzer (110) cites the work of Fotiyev (111) who found 85% of the material in swamp water to be fulvic acid. In soils the percentage of humic acid is considerably higher. According to Burges (31), the humic acid percentage is 75 to 80% for a Podzol soil and 40% for a Chernozem soil.

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Chemical Characterization of Aquatic Humics

The results of elemental analyses of aquatic humic fractions as reported by several independent workers are summarized in Table 9. A comparison of these results with similar ones for soil humic matter prompted Gjessing (112) to generalize that aquatic humics have lower carbon and nitrogen contents and higher hydrogen contents.

The nitrogen content in aquatic humics has received attention by Gjessing (112) who found no amino acids in the hydrolyzed products of aquatic humics. Gjessing also found that the more colored a water was (i.e. the more aquatic humics it contained) the less nitrogen it contained. This same observation, according to Gjessing, was made by Birge and Juday (113). These workers also felt that the nitrogen found arose mainly from analytical contamination; Gjessing, however, was unable to come to that same conclusion.

TABLE 9. ELEMENTAL ANALYSES OF AQUATIC HUMIC FRACTIONS

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Fraction	% C	% H	% N	% O	Ref.
Fulvic Acid	55.61	5.91	2.13	a	27
Fulvic Acid	54.87	5.56	2.41	a	27
Fulvic Acid	59.32	6.75	1.22	a	27
Fulvic Acid	58.42	6.18	1.26	a	27
Fulvic Acid	57.91	6.11	1.34	a	27
Fulvic Acid	57.08	6.47	2.17	a	27
Fulvic Acid	58.39	5.81	0.57	a	27
Humic Acid	29.30	5.94	1.85	62.91	18
Fulvic Acid	41.50	5.72	1.98	50.80	18
Hymatomelanic Acid	49.29	5.11	1.24	44.36	18
Fulvic Acid	46.20	5.90	2.60	45.30	29

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a: Not reported

Unfortunately no information was found in the literature on the percentages of functional groups present in aquatic humic fractions.

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Physical Characterization of Aquatic Humics

Spectroscopic studies with aquatic humics have involved the IR, UV, and X-ray regions of the electromagnetic spectrum. The IR region has provided the most information, being used by a number of workers (18,106,109,114) to obtain information on the functional groups present in aquatic humics. Lamar (113) found that the IR spectra of aquatic humics from distant, unrelated sources were strikingly similar. Shapiro (106) used X-ray diffraction in an attempt to determine structural characteristics of aquatic humics. He concluded that the material was amorphous. The sample he studied, however, represented total aquatic humics and was not divided into the classical fractions of Oden. Shapiro also used the UV region of the spectrum and found the region barren of any significant information. Black and Christman (17) also observed only end absorption in the UV region of the spectrum. Craige and McLachlan (115), on the other hand, working with marine humics, found the UV region useful.

Black and Christman (18) determined equivalent weights for ten samples of aquatic fulvic acid employing a nonaqueous titration in ethylenediamine. The equivalent weights for the ten samples studied by them ranged from 89 to 138.

The effect which pH has upon the color imparted to natural waters by the aquatic humics was, according to Shapiro (106), first investigated by Ohle (116) and Hutcheson (117). Shapiro found their results inconclusive and stated that increasing pH increased the color reversibly and almost linearly. Black and Christman (17) found a similar relationship between color and pH but concluded that the relationship was not linear. Christman and Ghassemi (16) carried the work a step further noting that the pH-color relationship was neither linear nor uniform for different colored waters. Interestingly, they also found that if the humic and hymatomelanic acid fractions were first removed (i.e. leaving only the fulvic fraction), the pH - color relationship became linear.

Solution fluorescence characteristics of aquatic humics were studied by Black and Christman (17). They found the wavelength of maximum emission unaffected by changes in pH, although emission intensity was affected. Also, at constant pH color value was linearly related to fluoresence intensity. Various solution fluoresence techniques as applied to aquatic humics are discussed in some detail by Christman and Arnquist (149).

Gjessing (112) provides a discussion on the use of gel filtration with Sephadex as a means of molecular weight determination. Shapiro (118) used Sephadex and determined the molecular weight of aquatic humic material in general (i.e. "yellow organic acids") to be approximately 10,000 and higher. Shapiro also found that, of the samples taken from 22 Minnesota lakes, four basic elution patterns resulted. He concluded from studying these elution patterns that they merely manifested the different proportions of aquatic humic fractions present in the various lakes. Shapiro also identified a definite relation between the molecular weight of aquatic humics and their ability to bind iron. High molecular weight humics were generally found to bind more than those of low molecular weight.

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Ghassemi and Christman (119) using Sephadex found an apparent molecular weight range for "organic color molecules" (i.e. aquatic humics) to be 700 to 10,000 relative to dextrans. One fraction was also found by them to have a molecular weight in excess of 50,000. For comparison they also present the results of Gjessing (120) who found molecular weights of 100,000 - 200,000 and 10,000 for two fractions of a typical Norwegian moorland water. Ghassemi and Christman also found that the molecular weight distribution of the aquatic molecules was a function of pH -- higher pH favoring higher molecular weights. It was proposed that at higher pH values the molecular weight increased due to complexation of the aquatic humics with iron or with other metallic hydroxides. Ghassemi and Christman also investigated the nature of iron - color association and the relationship of this association with pH. They found iron - color association to be highest in highly acid and highly alkaline pH regions with the acid regions yielding the higher iron - color association of the two. Relatively low iron - color association was observed at pH 7 - 8. They reasoned that at low pH values strong chelation between iron and color molecules occurs. As the pH is increased, hydroxide ion competes for the coordination sites of iron. At strongly alkaline pH values iron - hydroxo complexes become re-associated with the aquatic humics molecules through adsorption. Ghassemi and Christman point out that their findings are in conflict with those of Shapiro (118) who also studied iron-color association but found the association to be greatest for intermediate pH values.

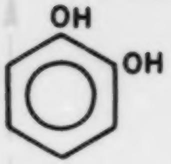
Rashid and King (121) used Sephadex to determine the molecular weight distribution of humic and fulvic acids in marine sediments. They found a non-uniform distribution of molecular weight of from 700 to over 2,000,000. They concluded from these results that the molecular weights of humic and fulvic acids of marine sediments were higher than those for soils. They labeled their results "tentative" as they were based on a limited number of measurements from only two marine areas.

Gjessing provides comments on the use of ultrafiltration as a technique for molecular weight determination of aquatic humics. Two examples of researchers using the technique are also cited (122,123).

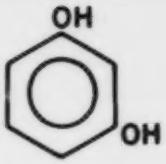
Structural Characterization of Aquatic Humics

The work of Christman and Ghassemi (16) represents the core of work available in the literature on the degradation and structural characterization of aquatic humics. These authors first concentrated aqueous organic color compounds by freeze concentrations and then effected a degradation of the concentrate via an alkaline - CuO technique. Their alkaline - CuO degradation was conducted at 175 - 180°C for three hours. Following this, the degradation products were separated and identified via thin-layer chromatography. Seven degradation products were identified; these are summarized in Figure 4.

The nature of the compounds identified concurred with the earlier data presented by Black and Christman (18) indicating organic color molecules to be aromatic in nature. These results, however, cast further doubt on the earlier conclusion drawn by Shapiro (106) that organic color molecules were predominantly aliphatic in nature.



Catechol



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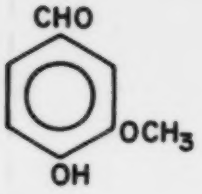
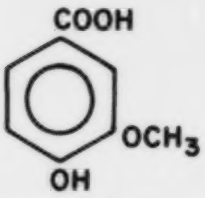
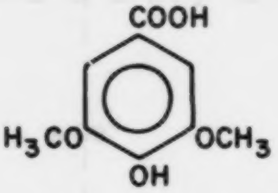


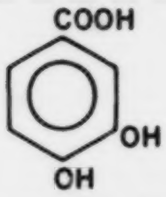
Vanillin



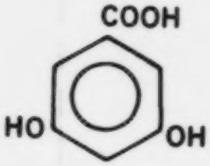
Vanillic Acid



Syringic Acid

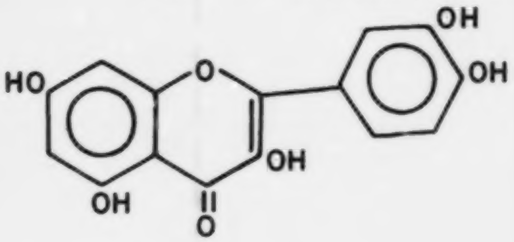


Protocatechuic Acid

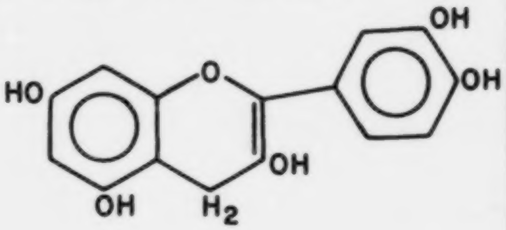


3, 5 - Dihydroxybenzoic Acid

Figure 4. Degradation products of aquatic humics (16).



Quercetin



Catechin

Figure 5. Other compounds extractable from wood (16).

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Christman and Ghassemi make the important observation that the identification of resorcinol and 3, 5-dihydroxybenzoic acid in the degradation products almost definitely preclude lignin being the sole precursor of aquatic humics as the m-dihydroxy substitution pattern has never been isolated in lignin. They hasten to point out, however, that other compounds, such as catechin and quercetin, Figure 5, having the m-dihydroxy substitution patterns can also be extracted from wood. The point is clearly made that lignin is undoubtedly not the only precursor of humics.

From the identified degradation products and the reactivity of model compounds subjected to the same alkaline - CuO oxidation conditions as the concentrated aquatic humics, intermonomeric linkages were hypothesized by Christman and Ghassemi. They also proposed a color macromolecule reproduced in Figure 6. This proposed molecule represents aquatic organic color in general and does not represent simply fulvic acid or simply humic acid as do certain soil humics models presented earlier in this review.

Humification as a General Process of Nature

The subject of microbial degradation and formation of humics from lignin has received an extensive treatment by Christman and Oglesby (124). The point is made at the outset of this work that biological agents are instrumental in humification of lignin. The primary organisms responsible for degrading lignin on the forest floor are the white rot fungi belonging to the class Basidiomycetes. Detailed metabolic/degradative pathways in the humification of lignin are presented. The general characteristics of humification of lignin are presented. Data indicating a decrease in methoxyl content and an increase in nitrogen content as humification proceeds are presented. In addition, a functional group analysis for a typical lignin and a humic acid are presented for comparison. Table 10 illustrates the comparison made. The most outstanding changes are increases in carboxyl and carbonyl and a decrease in methoxyl. The decrease in methoxyl is thought to be a result of the microbial degradation of the lignin. The increases in carbonyl and carboxyl are explained as likely being due to various oxidations of the products of the microbial degradation. Following these oxidations it is thought that the resultant highly reactive phenolic and quinonoid intermediates polymerize together with other polyphenols (from the microbial degradation) and amino acids to form humus. In summary, one begins with a large, poorly-defined molecule (lignin) and ends up with another large molecule (humus) even more amorphous than the starting material. It is as if the well-known tendency of nature to proceed to greater and greater disorder were manifesting itself once again. Figure 7 schematically illustrates the overall process thought to occur in the humification of lignin.

Christman and Oglesby point out that, based upon what is known about the chemical nature of humus, other chemical compounds (other than just those resulting from the degradation of lignin) must be involved in the formation of humus. The reader should recall that a similar conclusion was drawn by Christman and Ghassemi (16) after examination of the degradation products of aquatic humics. Christman and Oglesby after expressing this caveat explain that there was in any case little information in the current literature about metabolic pathways for products other than lignin.

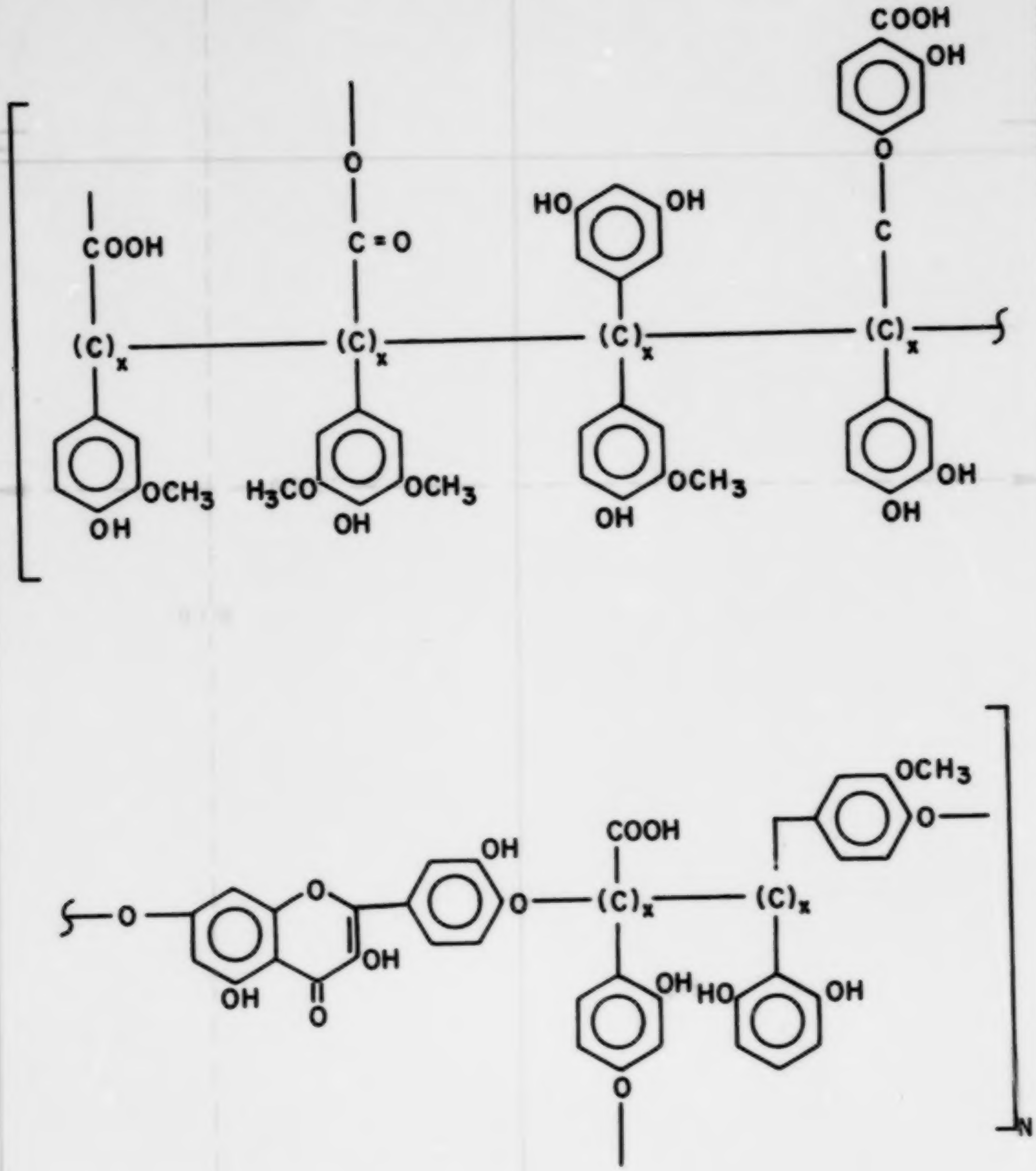
COOH
OH
O
C=O
HO
OH
O
C
COOH
(C)x
(C)x
(C)x
(C)x
OCH3
H3CO
OCH3
OCH3
OH
OH
OH
OH
OH
OCH3
OH
COOH
O
O
O
OH
OH
O
(C)x
(C)x
OH
HO
OH
O
N

Figure 6. Color macromolecule proposed by Christman and Ghassemi (16).

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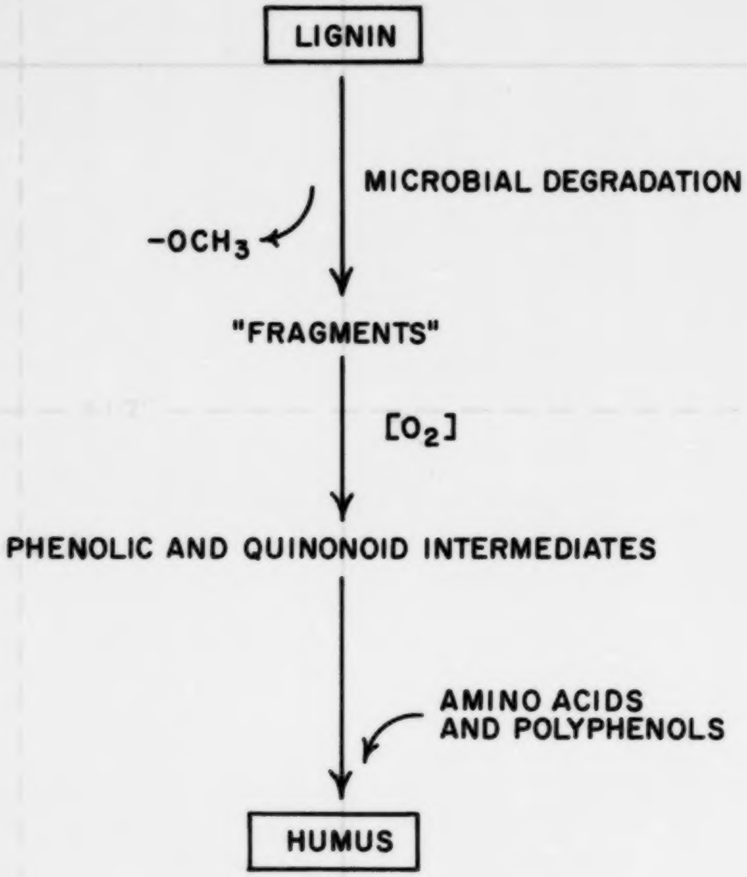
LIGNIN
MICROBIAL DEGRADATION
$-OCH_3$
"FRAGMENTS"
$[O_2]$
PHENOLIC AND QUINONOID INTERMEDIATES
AMINO ACIDS AND POLYPHENOLS
HUMUS

Figure 7. Schematic illustration of lignin humification (124).

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TABLE 10. COMPARISON OF FUNCTIONAL GROUP ANALYSES FOR LIGNIN AND HUMIC ACID (124)

	Lignin Millimoles/Gram	Humic Acid Millimoles/Gram
Methoxyl	5.1	0.2
Total Hydroxyl	6.2	5.1
Phenolic Hydroxyl	1.6	2.9
Alcoholic Hydroxyl	4.6	2.2
Carbonyl	1.0	5.5
Carboxyl	Trace	8.6

A work of related interest on the bacterial metabolism of methoxy compounds (125) and another on the bacterial degradation of phenolic compounds (126) were found by the current reviewers.

To assume that lignin is the sole precursor of humus is an oversimplification. Another tempting oversimplification is that humification occurs only in the soil. There is actually much evidence to the contrary. Knonova and Aleksandrova (127) for instance were able to observe humic substances produced by the fungi Aspergillus niger and Penicillum spp. utilizing glucose as a substrate. Craigie and McLachlan (115) observed that marine algae excreted humic type substances. Nissenbaum and Kaplan (128) were able to provide evidence that marine humic matter has its origin in the sea rather than by transport from terrestrial sources. They were able to show that marine humics were innately different from terrestrial humics on the basis of sulfur content and carbon-13 abundance. They further proposed that the pathway for the formation of marine humics was as follows: degraded marine cellular material → aqueous complex of carbohydrates and amino acids → fulvic acids → humic acids. Rashid and King (121) found humic acid and fulvic acid fractions in marine clays. Painter, et al. (129) in 1960 attempted to identify and classify the organic material present in sewage effluents and were unable to identify about 65%. The unidentified fraction later came to be identified by Rebhun and Manka (130) and Manka, et al. (131) as humic material. Sieburth and Jensen (132) studying the exudates of various seaweeds found that the exudates which were predominantly phenolic in nature went on to form polyphenols and eventually humic substances. Sieburth and Jensen, interestingly enough, found the same process (phenols to polyphenols to humics) occurring in bog water and the effluent of a paper mill. They proposed that it may be a common mechanism that forms both terrestrial and marine humic substances.

That humification is a general process of nature is an underlying theme in the relatively recent review paper by Jackson (133). Jackson at one point makes the comment: "Humification is a major geochemical phenomenon of great importance to the biosphere." The point is made that the accumulation of humic matter over geologic time is responsible for the coal and oil reserves available today. Jackson states that the holding of such tremendous amounts of carbon in a relatively inert state (i.e. as humic substances or fossil fuels) rather than allowing them to be oxidized may in part be the reason that large concentrations of oxygen were able to be built up in the atmosphere. Humic substances may be responsible for the concentration of metals in the earth's crust as also discussed earlier in the review. Jackson also states that humic substances in natural waters may make available trace nutrients such as Fe^{3+} or may assist in the removal of toxic metals by a scavenging. Evidence that humics may even scavenge harmful organic pollutants of man-made nature is discussed. Jackson even speculates that humic substances in natural waters may through influence on pH, toxins, nutrients, etc. be instrumental in successions of species that take place commonly enough in all natural waters. Calling upon the fundamental principal of natural science that nature doesn't do anything without a purpose, Jackson speculates that this may then be the reason that seemingly wasteful quantities of humic substances are produced by algae. Humics in natural waters may in fact be essential for life on earth. Humification may be not only a general process of nature but also an essential one.

REACTIONS OF PHENOLIC MATERIAL WITH CHLORINE

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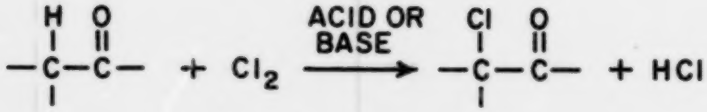
It is well recognized (134,135,136) that chlorine is capable of substituting for hydrogen in aliphatic molecules containing an enolizable ketone. The attack involves the carbon alpha to the carbonyl and is catalyzed by either acids or bases. The rate of this reaction is proportional to the concentrations of ketone and of added acids but is independent of the concentration of chlorine. The rate controlling step involves the formation of the enol and the following mechanism is supported by experimental observations that the rate of chlorination of ketones with optically active alpha carbon atoms is identical to the acid catalyzed rate of racemization.



$$-\overset{H}{\underset{|}{\overset{|}{C}}}-\overset{O}{\overset{\|}{C}}- + Cl_2 \xrightarrow{\text{ACID OR BASE}} -\overset{Cl}{\underset{|}{\overset{|}{C}}}-\overset{O}{\overset{\|}{C}}- + HCl$$

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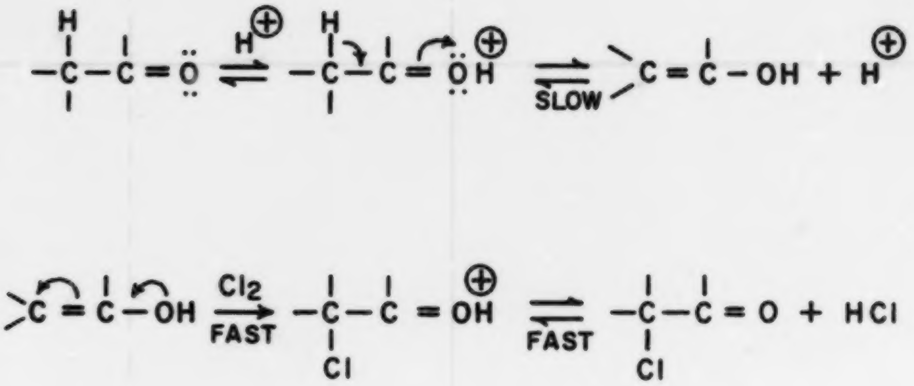
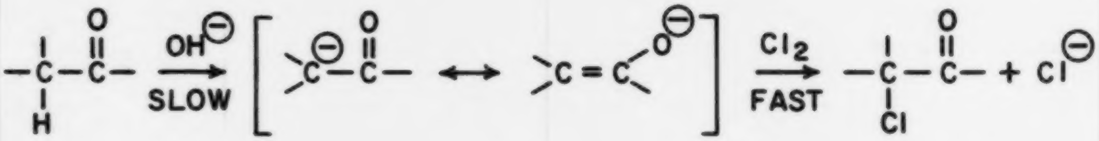


In basic solution the reaction rate is also independent of halogen although the first and rate controlling step is different, involving the removal of a proton from the ∝-carbon.



For unsymmetrical ketones, substitution occurs exclusively on the more heavily substituted ∝-carbon under acid conditions since the enol form of the more substituted double bond is more stable. Under basic conditions, the reverse is true due to the greater stability of the less heavily substituted carbanion. In either case successive halogenation proceeds rapidly and terminates with the location of three halogens atoms on the ∝-carbon.

Trihalomethyl ketones are unstable in the presence of base and are cleaved to a trihalomethane and the corresponding acid (haloform reaction). Morris (137) has pointed out that the potential precursors for the haloform reaction include, in addition to methyl ketones, those structures which can be converted to methyl ketones, such as ethanol, acetaldehyde, secondary alcohols and unsaturated compounds of the type $CH_3CH=CR_1R_2$.

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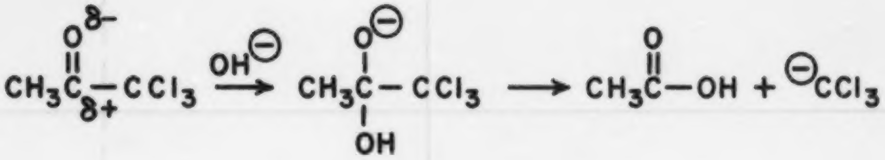
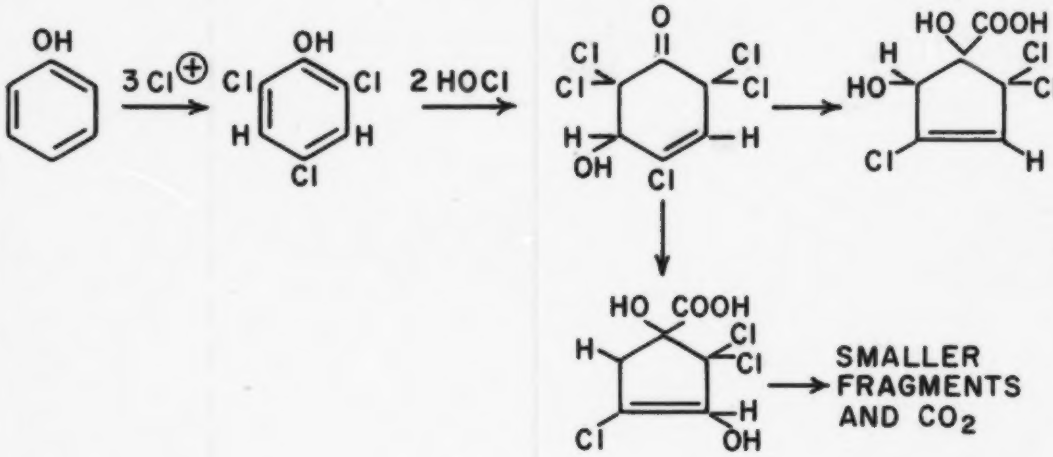


$$CH_3\overset{O^{\delta-}}{\overset{\|}{C}}_{\delta+}-CCl_3 \xrightarrow{OH^{\ominus}} CH_3\underset{OH}{\overset{O^{\ominus}}{C}}-CCl_3 \longrightarrow CH_3\overset{O}{\overset{\|}{C}}-OH + {}^{\ominus}CCl_3$$

The substitution of chlorine into the aromatic nucleus is enhanced by the presence of ring activating substituents such as the hydroxyl, methoxyl and amide groups, which preferentially direct halogen substitution to the ortho and para positions (134-137). Beyond direct substitution chlorine (and bromine) will degrade the aromatic nucleus yielding 5-membered rings initially (138) and smaller fragments ultimately (137). Moye (138) notes that simple phenols and many mononitrophenols yield large quantities of $CHBr_3$ and CBr_4 under conditions of the bromopicrin reaction.



Considerable research has been conducted on the chlorination of lignin and lignin model compounds because of the importance of chlorine and hypochlorite bleaching in the pulp manufacturing process (139). This process

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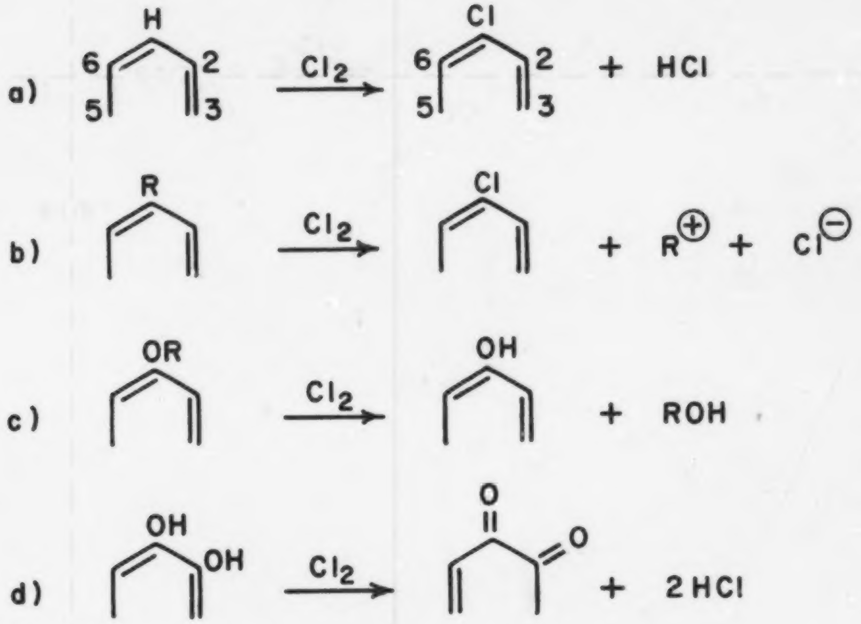
generally employs acid prechlorination (pH 2) of digested pulp fibers which renders the bulk of the residual lignin soluble in both water and alkali. Most of the fiber color improvement results from a subsequent hypochlorite bleaching state (pH 8-9). According to Sarkanen (139), the reactive chlorine species in acid lignin bleaching is molecular chlorine while in hypochlorite bleaching HOCl, or a reactive intermediate derived from it, plays the primary role in attacking lignitic structures.

In acid conditions chlorine atacks the phenylpropanoid nuclei of lignin molecules in several ways (139,140,141). In approximate order of decreasing reaction rate these include a) direct substitution of hydrogen on the aromatic ring, b) electrophillic displacement of the alkyl side chain, c) hydrolysis of aryl ether linkages and d) oxidation of o-dihydroxy groups to o-quinones.



Additional reactions may include reactions with the propanoid side chain (141), such as addition of HOCl across double bonds and chlorine substitution for hydrogen or carbon atoms alpha to carbonyl groups.

Initial chlorine substitution in the aromatic ring (reaction [a]) is quite rapid (139) although the specific carbon atom attacked depends on the nature of the other ring substituents including the alkyl side chain (141). Most of the common ring substituents in lignin and in lignin models are o-p directing (OH, OCH_3). The only notable exception is a carbonyl group

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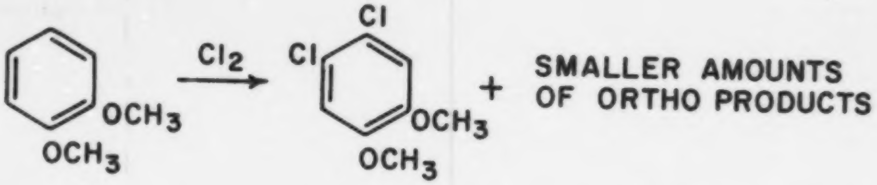
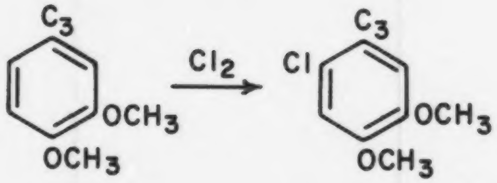
alpha to the ring which is a strong meta director. The hydroxyl group is a stronger influence than the methoxyl group and para direction dominates ortho direction so that with regard to ordinary aromatic substituents in lignin aromatic rings;

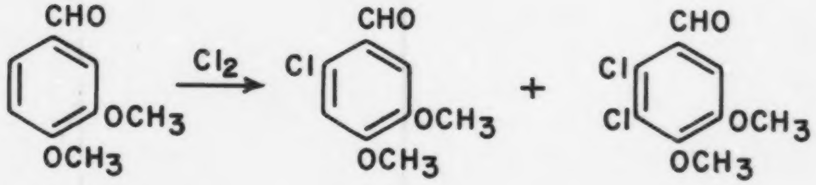
$$\underline{p}\text{-OH} > \underline{p}\text{-OCH}_3 > \underline{o}\text{-OH} > \underline{o}\text{-OCH}_3$$

Thus, veratrole (1, 2-dimethoxybenzene) is chlorinated predominantly at the 4 and 5 positions with concentrations of the $\underline{o}$-chloroveratrole product representing 1/80 of the $\underline{p}$-product. If the 4 position in veratrole is blocked by a propanoid


Cl_2
Cl
Cl
OCH_3
OCH_3
OCH_3
OCH_3
+
SMALLER AMOUNTS OF ORTHO PRODUCTS

side chain, substitution occurs solely at the 5 position unless the α position of the side chain contains a carbonyl which would increase the amount of substitution at the 6 position. Guaiacyl derivatives more strongly favor substitution at the 5 position because of the greater influence of hydroxyl relative to methoxyl. In the case of syringyl derivatives the 2 and


C_3
Cl_2
Cl
C_3
OCH_3
OCH_3
OCH_3
OCH_3


CHO
Cl_2
Cl
CHO
+
CHO
Cl
Cl
OCH_3
OCH_3
OCH_3
OCH_3
OCH_3
OCH_3

6 positions are equally activated and substitution occurs with equal facility

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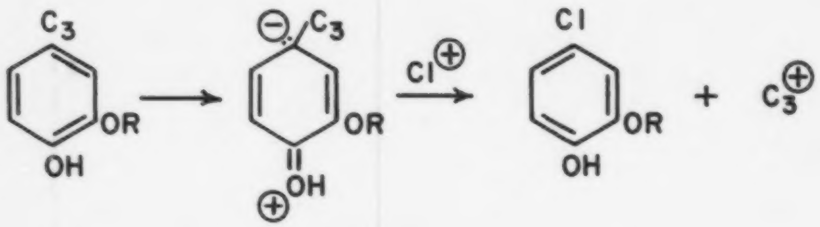
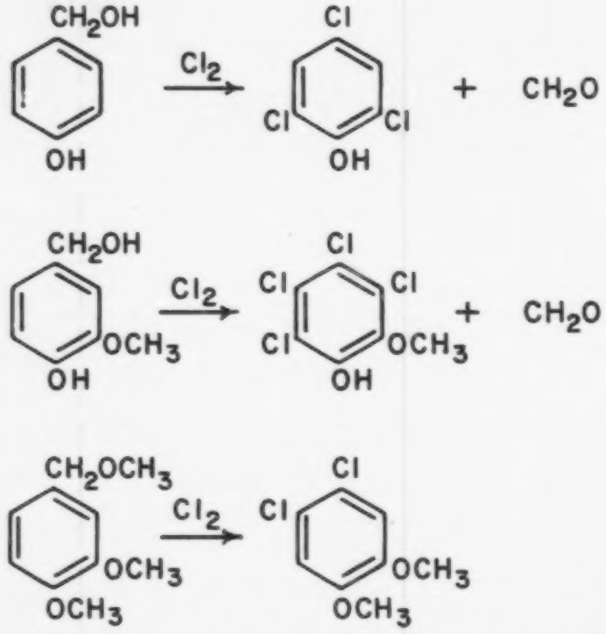
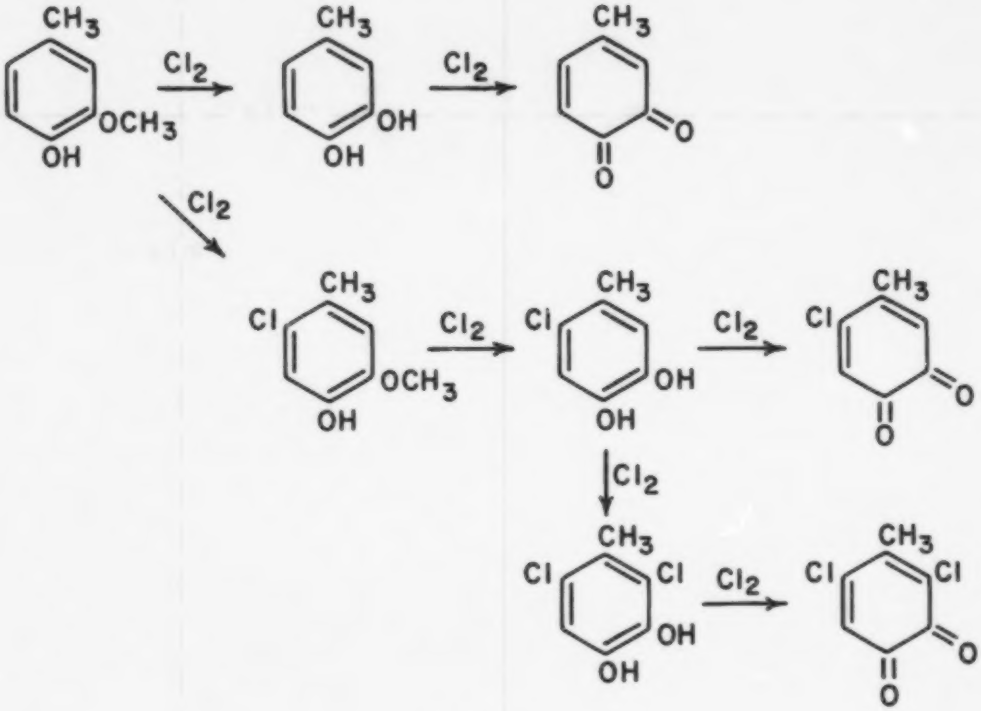
at either site.

Electrophilic displacement of the alkyl side chain occurs most readily (140,141) when the hydroxyl group at position 4 is free and, therefore, contributes to activation of the ring at the number 1 position. Methoxyl groups activate this position less strongly. Data of Sarkanen and Dence (142) presented in Dence's review (141) suggest that the rate of side chain replacement is also accelerated when the α-carbon of the side chain is hydroxylated or alkoxylated.


C3
OR
OH
C3
OR
OH
Cl⊕
Cl
OR
OH
+
C3⊕


CH2OH
OH
Cl2
Cl
Cl
Cl
OH
+
CH2O
CH2OH
OCH3
OH
Cl2
Cl
Cl
Cl
Cl
OCH3
OH
+
CH2O
CH2OCH3
OCH3
OCH3
Cl2
Cl
Cl
OCH3
OCH3

The ability of chlorine to hydrolyze aryl ether linkages is one of the oldest known and commercially successful processes in the pulp and paper industry. The principal result is a decrease in lignin methoxyl content and a corresponding increase in free MeOH which is commercially recoverable from bleach plant liquor (139-141). Gess and Dence (143) have shown that the 3, 4-dihydroxylphenolic configurations resulting from the hydrolysis of guaiacyl units are subsequently oxidized to o-quinones. The combination of aromatic substitution, aryl ether hydrolysis and dihydric phenol oxidation reactions can lead to a variety of reaction products.



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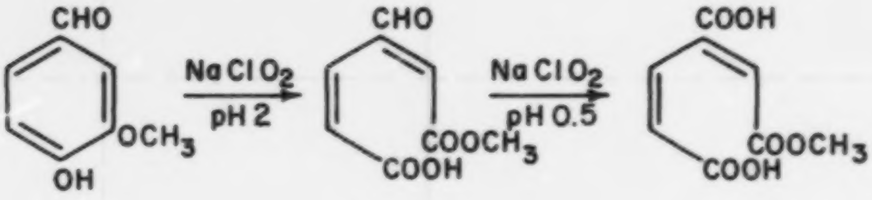
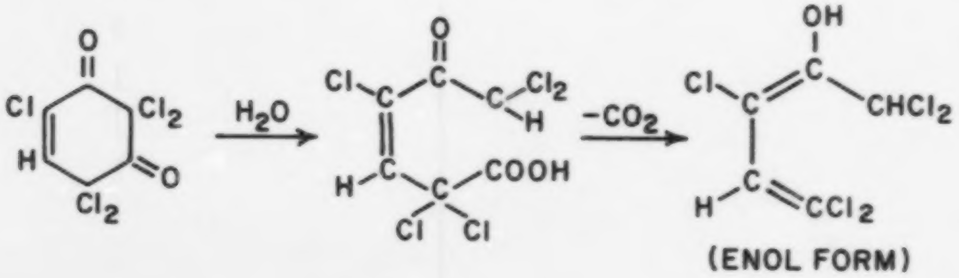
Less is known about the reactions of lignin model compounds in hypochlorite solutions. Sarkanen (139) notes that the rate of the chlorination reaction in neutral and alkaline solution is proportional to the phenolic and HOCl concentrations and that an optimum pH exists according to:

$$pH = 1/2\ (pK_{phenol} + pK_{HOCl})$$

Under these conditions lignin models undergo all of the above reactions with the exception of aryl ether hydrolysis. Although the action of chlorine dioxide is less well known it appears that the reaction products contain less substituted chlorine and greater carboxylic acidity due to cleavage of the aromatic ring (144,145). Loss of methoxyl occurs with chlorine dioxide as readily as with chlorine.



None of the reactions investigated in lignin or lignin model halogenation studies have established the production of any specific halomethane, although the potential exists via the haloform mechanism considering the number of enolizable carbonyl groups in the many reaction products. In fact, the production of trihalomethanes even from simple phenols has not been accounted for mechanistically. Most recently Rook (146) has called attention to the finding of Moye (147) that pentachlororesorcinol forms a diene which is unstable in water decarboxylating to form 1, 1, 3, 5, 5-pentachloropent-4-en-2-one.



According to Rook it is attractive to assume that this product or a similar one formed by hydrolytic cleavage at the 1-2 position will lead to $CHCl_3$.

SECTION 4

HUMIC ISOLATION PROCEDURES

Experiments were performed on humic material isolated from Black Lake, a highly colored (574 Pcu), soft (Ca^{++} <1.0 mg/L) surface water located on the N.C. coastal plain near Elizabethtown, N.C. A partial chemical analysis of this water appears in Table 11.

Two isolation procedures were used to obtain humic material from Black Lake, the first of which is shown in Figure 8. Samples of Black Lake water ranging from 200 to 500 gal. were filtered through a 10 µm polypropylene honeycomb filter and acidified to pH 2.2 with HCl to precipitate a combined

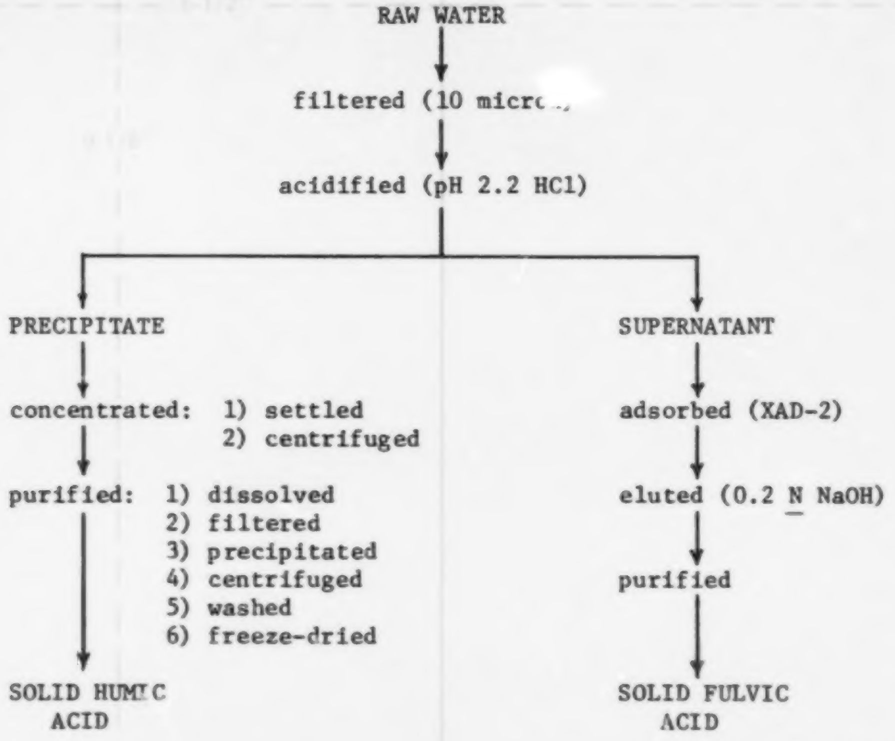

RAW WATER
filtered (10 micr
acidified (pH 2.2 HCl)
PRECIPITATE
SUPERNATANT
concentrated: 1) settled
2) centrifuged
purified: 1) dissolved
2) filtered
3) precipitated
4) centrifuged
5) washed
6) freeze-dried
SOLID HUMIC ACID
adsorbed (XAD-2)
eluted (0.2 N NaOH)
purified
SOLID FULVIC ACID

Figure 8. Isolation of aquatic humic material.

TABLE 11. PARTIAL CHEMICAL ANALYSIS OF BLACK LAKE WATER*

Calcium	<1.0 mg/L	Chloride	18 mg/L
Magnesium	<0.5 mg/L	Sulfate	18 mg/L
Zinc	<0.01 mg/L	Nitrogen	
Copper	0.02 mg/L	Nitrate-N	0.020 mg/L
Iron	0.7 mg/L	Nitrite-N	0.015 mg/L
Manganese	0.14 mg/L	Ammonia-N	0.135 mg/L
Sodium[+]	18 mg/L	Phosphorus	
		Total	1.85 mg/L
		Dissolved	0.95 mg/L
		Orthophosphate	0.02 mg/L

Color	574	Platinum Cobalt Units at pH 6.5
pH	6.5	
Total Solids	144 mg/L	
Suspended Solids	20 mg/L	
Total Alkalinity	13 mg/L as $CaCO_3$	
Surface Area	1418 Acres	
Max. Depth	Ca 6 ft.	
Total Organic Carbon	range, 15-25 mg/L, ave. 18.2 mg/L	

*mg/L as reported species unless otherwise indicated

[+] estimated by difference, meqCl^- + meq $SO_4^=$ - meq Cations

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humic-hymatomelanic acid fraction which was concentrated by settling and centrifugation at 2000 rpm for one hour. The actual purification procedures varied slightly for materials used in $KMnO_4$ and Cl_2 oxidation experiments, as noted in these sections respectively. In general the following steps were used. The humic-hymatomelanic acid pellet was redissolved in a NaOH solution, filtered through glass wool or fiber, reprecipitated with concentrated HCl, and recentrifuged. The resulting pellet was washed with either HCl solution (pH 2) or distilled water and again centrifuged. These processes were repeated several times depending on the sample. The final pellet was freeze-dried to a solid.

The supernatant containing organic material soluble at pH 2.2 was passed through a column containing from 1 to 2 L of XAD-2 resin under conditions outlined by Mantoura and Riley (150). The resin was cleaned prior to use by sequential washings with 1 N HCl and 1 N NaOH followed by 8 hour soxhlet extraction with each of three solvents: ethyl ether, acetonitrile or acetone, and methanol. Organic material was eluted from the resin in 0.2 N NaOH (fulvic acid fraction) after passage of about 50 gal. of supernatant. Gel filtration profiles on both fractions were typical of the size distribution of aquatic humic and fulvic acid materials (Figure 10). Further purification of the fulvic acid fraction will be described in greater detail in following sections.

The utility of using triethylamine instead of sodium hydroxide as a base in the humic preparation procedure was evaluated. Using this method Reuter (151) was able to produce a very soluble material containing no ash. It was felt that a reduced ash content could increase the yields of various degradation reactions.

A sample of Black Lake water was filtered as before and acidified to pH 1.7 with HCl (Figure 9). The precipitated humic-hymatomelanic acid fraction was then concentrated by settling and centrifugation. This solid humic material was dissolved in a solution of 3% triethylamine which was freshly redistilled. The solution was allowed to sit for 24 hours to ensure complete dissolution and was then centrifuged to remove any insoluble material.

The humic-hymatomelanic acid solution was divided into two equal fractions A and B. Fraction A was extracted with chloroform for 24 hours in a continuous liquid-liquid extractor to remove any triethylamine hydrochloride. Fraction B was placed on a roto-evaporator for 2 hours in an attempt to remove excess triethylamine and then extracted as A was. The evaporator was not successful in triethylamine removal. Both fractions were then freeze-dried to solids.

The dissolved organic material in the Black Lake water supernatant was concentrated by passage through XAD-2 as before but this time the column was eluted with 3% triethylamine solution. This solution was roto-evaporated (very little solution removed) and extracted with chloroform as with the humic solutions. Quantities of the cation exchange resin Biorad AG 50WX8 were then added to remove metal ions from solution. This step was attempted with the humic-hymatomelanic fraction but the rapid pH drop to about pH 2.5 caused precipitation of humic material which made it impossible to filter out

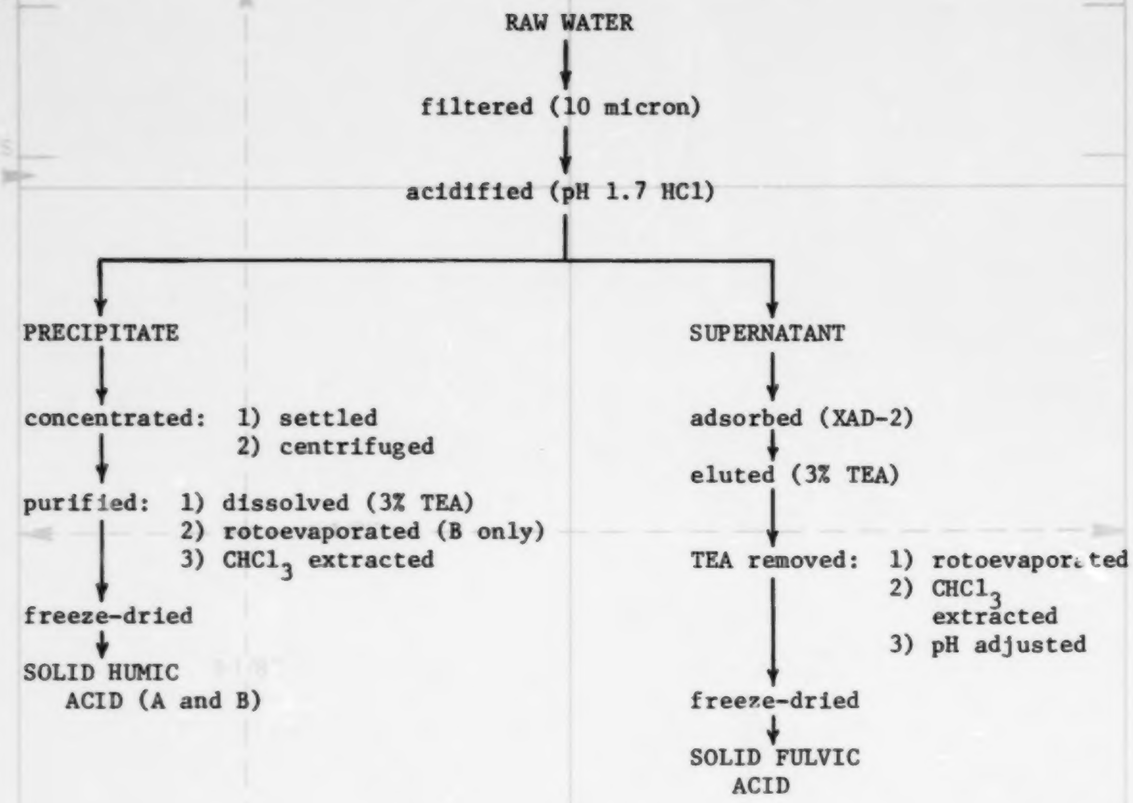
RAW WATER
filtered (10 micron)
acidified (pH 1.7 HCl)
PRECIPITATE
concentrated: 1) settled
2) centrifuged
purified: 1) dissolved (3% TEA)
2) rotoevaporated (B only)
3) CHCl3 extracted
freeze-dried
SOLID HUMIC ACID (A and B)
SUPERNATANT
adsorbed (XAD-2)
eluted (3% TEA)
TEA removed: 1) rotoevaporated
2) CHCl3 extracted
3) pH adjusted
freeze-dried
SOLID FULVIC ACID

Figure 9. Triethylamine isolation procedure.

the resin particles. After filtering the resin particles from the fulvic solution freeze-drying was employed to reduce the solution to a solid.

Elemental and ash analyses were done on humic-hymatomelanic and fulvic acid fractions from the triethylamine procedure and the humic-hymatomelanic fraction from the NaOH procedure. Results are presented in Table 12. It was concluded that the triethylamine procedure and its variations had no effect on the ash content of the humic or fulvic acids from Black Lake. Increased solubility of the humic-hymatomelanic acid fraction was observed but was believed due to the lingering presence of triethylamine in some form.

Three samples of humic material were prepared and delivered to MERL under a separate agreement. The sources of these were Black Lake, Lake Drummond (Great Dismal Swamp), and Lake Sagamore (N.Y.). Humic and fulvic material were prepared in each case by the procedure outlined in Figure 8. However, the fulvic acid was further purified by dialysis using membranes of molecular weight 1000 retention for 3 to 5 hours against distilled water. This dialysis procedure was repeated three times.

TABLE 12. HUMIC ELEMENTAL ANALYSIS

	% C	% H	% N	% Ash (by wet ignition w/H_2SO_4)
Humic A	50.71	7.05	5.84	12.03
Humic B	50.14	6.74	5.61	12.86
Fulvic	49.57	4.39	2.00	5.03
Humic (NaOH)	44.97	4.21	2.39	10.50

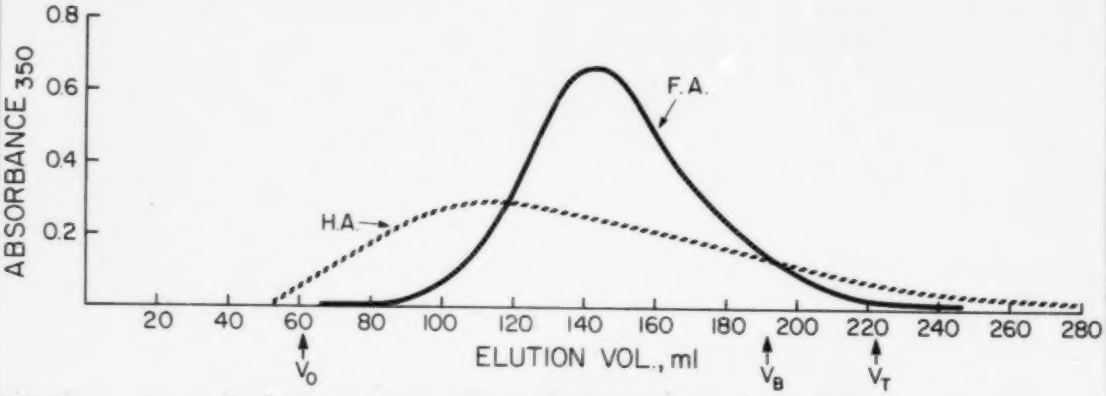

Figure 10. Gel filtration of aquatic humic material on Sephadex G-100 with a borate buffer, pH 9.9.

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SECTION 5

GC/MS PROCEDURES

The primary technique used for the identification of humic/fulvic acid degradation products was combined gas chromatography/mass spectrometry (GC/MS). Preliminary stainless steel packed column GC analyses using a flame ionization detector established that OV-17 as a liquid phase gave superior separating power when compared to OV-101, OV-210, OV-225 or Dexsil 410. Thus OV-17 on chromasorb W/AW was used for all GC/MS analyses. The mass spectrometer initially available for this work was a Finnigan 3300 quadrupole instrument interfaced to a Finnigan 9500 GC with data aquisition and processing by means of an INCOS 2300 data system. The mass spectrometer was found to give 2M resolution as measured by the full width at half maximum (where M is the mass) over the mass range of 28 to 414 daltons. Depending upon the degree of contamination of the analyzer, the resolution at higher mass was somewhat reduced so that some sensitivity could be retained. The mass spectrometer was scanned linearly from m/z 40 to 800 in 3.9 seconds with 0.1 seconds reset time The system was calibrated using FC-43 through m/z 614. Mass assignments to Ca. 700 were typically better than -0.2 daltons. Sensitivity consideration and the generally limited performance of the quadrupole mass filter led us to use double-focusing mass spectrometers when these became available. The later results were obtained on either a VG-micromass ZAB-2F of a VG-micromass 70.70 F high resolution mass spectrometer. The ZAB-2F is interfaced to a Varian 1400 GC and operated under the control of the INCOS data system. Mass analyzed-ion kinetic energy (MIKE) spectra were obtained using this instrument scanning the electric sector from OV through the main beam energy at 10 ms/eV. Helium at ca. 10^{-3} torr in the collision cell led to the attenuation of the main beam by 50% and the formation of collision-induced dissociation product-ions. Low resolution mass spectra were typically obtained by operating the instrument at 1000-2000 resolving power (10% valley definition) and scanning exponentially at 2-3 seconds/decade in mass from m/z 600 to 40 with 1 second for reset to give a scan cycle time of 3.5 - 4.5 seconds. The 70.70 F was interfaced to a Perkin-Elmer Sigma 3 GC and operated under the control of a VG-micromass 2035 F/B data system. This instrument was typically operated at 3000 resolving power (again, 10% valley) with a 3 second/decade exponential scan from m/z 600 to 22 with magnet reset time ca. 0.8 seconds to give a scan cycle of ca. 5 seconds. By using an internal reference compound and the VG-micromass real-time accurate mass measurement software, exact mass assignments were possible. Perfluorokerosene (PFK) was found to be undesireable for use with the hydrogen deficient, highly oxygenated compounds in the degradation products because many low intensity PFK peaks were not resolved from the sample peaks at 3000 resolving power. Tetraiodoethylene (TIE) has very few peaks in its mass spectrum and has a greater negative mass defect than PFK peaks so that it offers less chance of interference with the sample ions. Thus mass measurement accuracy improved from ca. ±15 ppm with TIE. This, of

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course, reduces the ambiguity in the assignment of elemental compositions. Chemical ionization mass spectra were obtained on all of the spectrometers typically using CH_4 as the reagent gas. The CH_4 pressure and extractor voltages were adjusted to maximize the ratio of m/z 29:m/z 27. Sample introduction was again via GC. The ion source was operated with no auxillary heating giving ca. 120°C for the Finnigan and 180°C for the VG-micromass instruments.

As can be seen by examination of typical total ion current plots from a GC/MS runs presented in later sections of this report, these samples are quite complex with many chromatographic peaks. The situation is even more complicated than this since many of the chromatographic peaks in fact contain two or three components. In the face of the rather large quantity of data it was decided to concentrate on preliminary identifications based upon interpretation of the mass spectral data with confirmation by means of gas chromatographic properties to follow as reference compounds became available. Also, the data analysis procedure evolved as our experience with these samples increased and more sophisticated instrumentation became available. What will be described are the methods as finally developed. Notations in the results will indicate which steps were used in the identification of a particular degradation product. The flow chart for our identification scheme is shown in Figure 11. In the interpretation of the low resolution EI data, we made appropriate use of the 25,000 spectrum library in the INCOS data system. The results of the library searches were occasionally found to be useful for guidance in the further interpretation of the data. In no case was a library match line valid as even a tentative identification. In the course of interpretating mass spectra of unknown compounds, considerable speculation is unavoidable and even desirable. However, in reporting results to investigators not expert in the handling of such data it is imperative to carefully distinguish between what we think and what we really know. Thus a short philosophical discussion on the subject of trace organic compound identification is in order.

For all degradation products reported, we know the masses of major ions produced by EI. This gives us at least a reasonable certainty of such properties as aromatic/aliphatic nature, at least some of the functional groups present, etc. In those cases in which both CI and exact mass (= high resolution) data are available we can be certain of the molecular weight and elemental composition. The availability of elemental compositions for fragment ions greatly enhances the confidence we can place in functional group/labile group assignments (it is much more satisfying to know that a molecular ion lost C_2H_3O than 43 daltons). Even with complete high resolution EI and CI spectra available, mass spectrometry generally does not allow the differentiation among closely related compounds. In those cases in which all the isomeric compounds are present in a given sample some *a priori* assumptions about GC properties may permit a more certain structural assignment. However, final structural assignment in all cases should not be made until reference standards are available.

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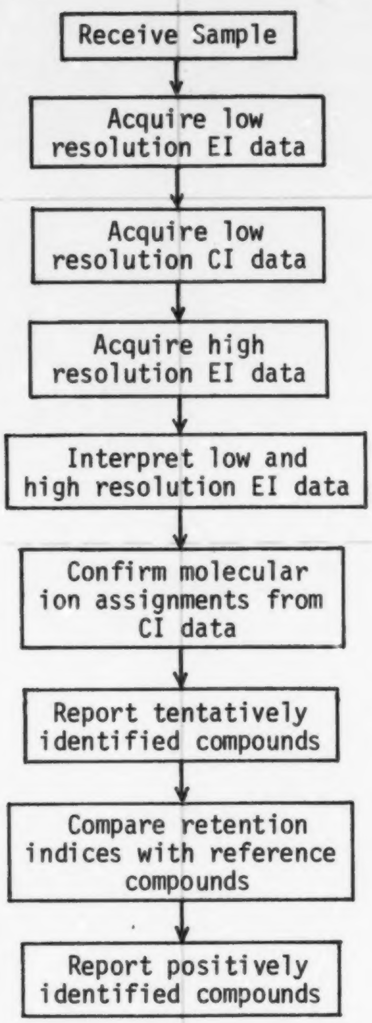
Receive Sample
Acquire low resolution EI data
Acquire low resolution CI data
Acquire high resolution EI data
Interpret low and high resolution EI data
Confirm molecular ion assignments from CI data
Report tentatively identified compounds
Compare retention indices with reference compounds
Report positively identified compounds

Figure 11. Flowchart for GC/MS identification of degradation mixtures.

SECTION 6

HUMIC CHARACTERIZATION EXPERIMENTS

PURIFICATION OF AQUATIC HUMIC SAMPLES

The aquatic humic materials that have been isolated according to Oden's classification into humic/hymatomelanic acids (HA) fraction and fulvic acids (FA) fraction are further purified by filtration and dialysis. The HA fraction was redissolved in 0.1 N NaOH, filtered through a glass wool filter, reprecipitated at pH 2 and freeze-dried. The concentrated FA fraction was filtered and reacidified to pH 5. Both HA and FA were transferred to dialysis bags and dialyzed for three days against distilled water to remove salts and non-humic organics. The HA was then freeze-dried. The ash content can be reduced to less than 5% in this manner.

GENERAL CHARACTERIZATION OF AQUATIC HUMIC SUBSTANCES

Elementary Analysis

Elementary analysis provides information on the quantitative elemental composition of humic substances. The results of analysis (Table 13) performed on aquatic humic samples prepared as above show that carbon, hydrogen, and oxygen are the major elements in humic molecules and HA's have a C:H:O ratio approximately 9:9:6 and FA's have a C:H:O ratio 8:7:6. The C:H:O ratio of humic substances can be used as a measure of the degree of unsaturation as well as a measure of the state of oxidation. The data indicate that FA's are in a higher oxidation state than HA's. Compared to soil humics, humic substances in waters contain less carbon and nitrogen.

TABLE 13. PERCENT ELEMENTAL COMPOSITION OF AQUATIC HUMIC SUBSTANCES

	C	H	N	O	Ash
HA (Black Lake)	48.04	4.49	2.56	40.40	4.50
HA (Lake Drummond)	48.80	4.02	2.54	39.85	4.79
FA (Black Lake)	46.67	3.52	1.34	44.13	4.32
FA (Lake Drummond)	45.83	3.31	1.24	45.25	4.37

Infrared Spectrophotometry

Spectrophotometric studies with aquatic humic substances involve the IR, UV, and X-ray regions of the electromagnetic spectrum. The IR region provides the most information on the distribution of functional groups. IR spectra of aquatic humics show similar patterns to those of soil humics. The representative spectrum (Figure 12) reveals that aquatic humics are complex polymeric substances containing a significant amount of oxygen-containing functional groups (CO_2H, OH and C=O).

IR spectrophotometry is useful for the gross characterization of humic materials and for the evaluation of chemical modifications such as the formation of derivatives, but it tells very little about the "building block" of the humic structures.

Nuclear Magnetic Resonance Spectrometry

NMR, a nondestructive method, has been exploited in one study of humic substances. The information obtained from ^1H NMR is pertinent to the distribution of aromatic, aliphatic, and other functional hydrogens present in humic molecules. ^{13}C NMR makes use of the signals recorded from the small proportion of ^{13}C in naturally occurring substances. The large chemical shift, recorded by this technique allow signals to be resolved for individual carbon atoms with only slightly different magnetic environments. The information obtained on the carbon skeleton of humic substances is very helpful for our degradation studies and allows for more interpretation on data available.

The dry humic acids that have been purified through dialysis were washed two times with 99.9% deuterated water. The samples were dried and then dissolved in 0.1 N NaOD solution for NMR analysis.

Both ^1H and ^{13}C spectra were obtained at 100 and 25.2 MHZ, respectively, on a Varian XL-100 Fourier transform NMR spectrometer interfaced with a mini-computer. ^1H NMR spectra were acquired using a 90° pulse and a total pulse delay and acquisition time at 0.5-1 second. For ^{13}C NMR, in addition to a 90° pulse used, a second radio-frequency field was applied for full proton spin decoupling. The free induction decay data were collected for 0.2-0.4 second. Multiple transients (500-200,000) were acquired locking onto the deuterium signal. The ^1H NMR spectra of Lake Drummond HA and FA are presented in Figures 13 and 14, respectively. The broad resonances between 0.8-1.8 ppm are characteristic of protons on carbons adjacent to functional group such as carboxyls and aromatics. Both spectra also show strong resonances in the 3.4-4.4 ppm range characteristic of protons on carbons attached to oxygen atoms, and in the 6.5-8.0 ppm region characteristic of aromatic protons.

The proton-decoupled ^{13}C NMR spectra of Lake Drummond HA and FA are presented in Figures 15 and 16, respectively. The spectra are encouraging and their resolution allows for a great deal more structural interpretation than previously possible. The types and relative amounts of carbon corresponding to each resonance region are also shown in Figures 15 and 16.

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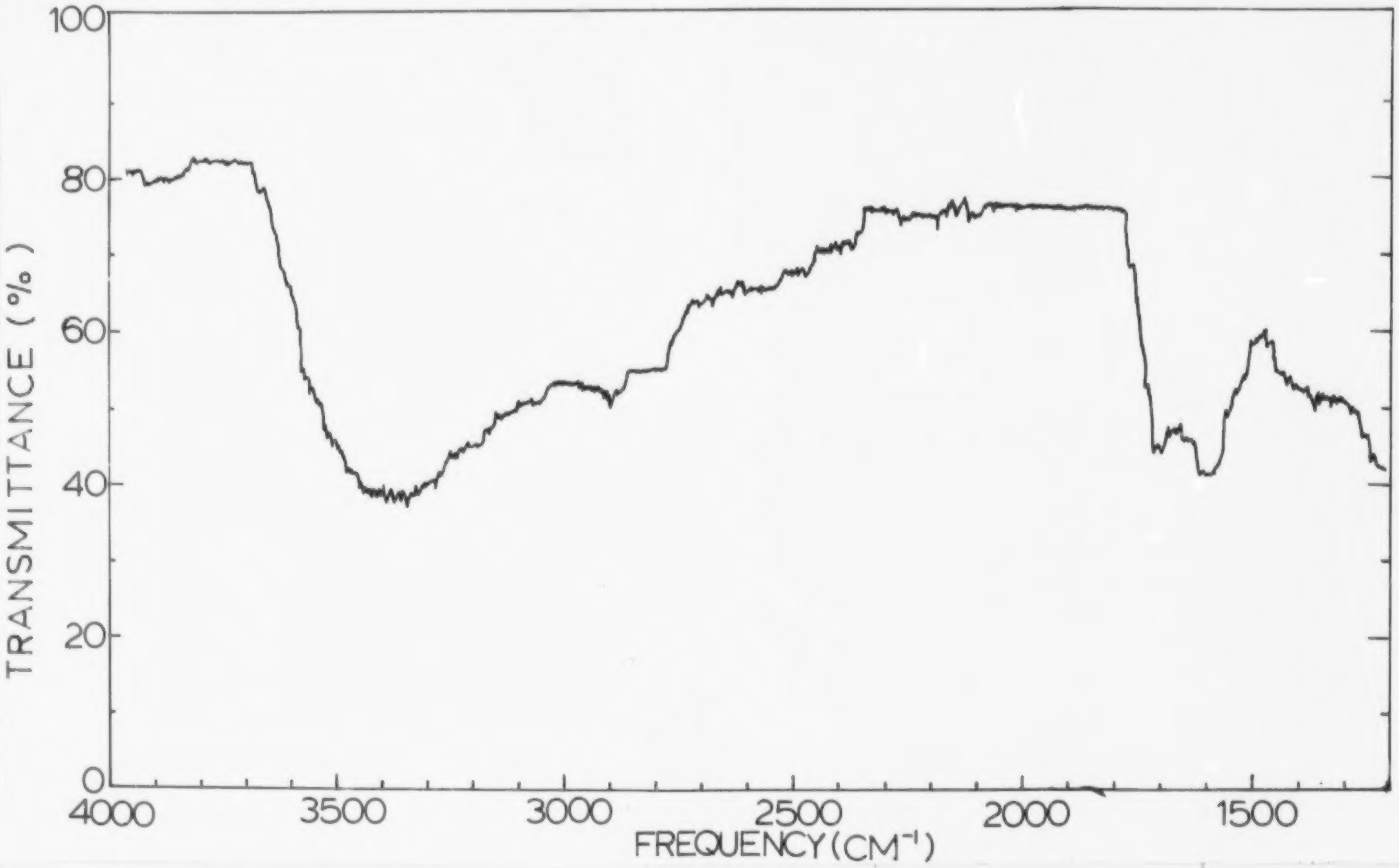

Figure 12. Infrared spectrum of aquatic humic acid.

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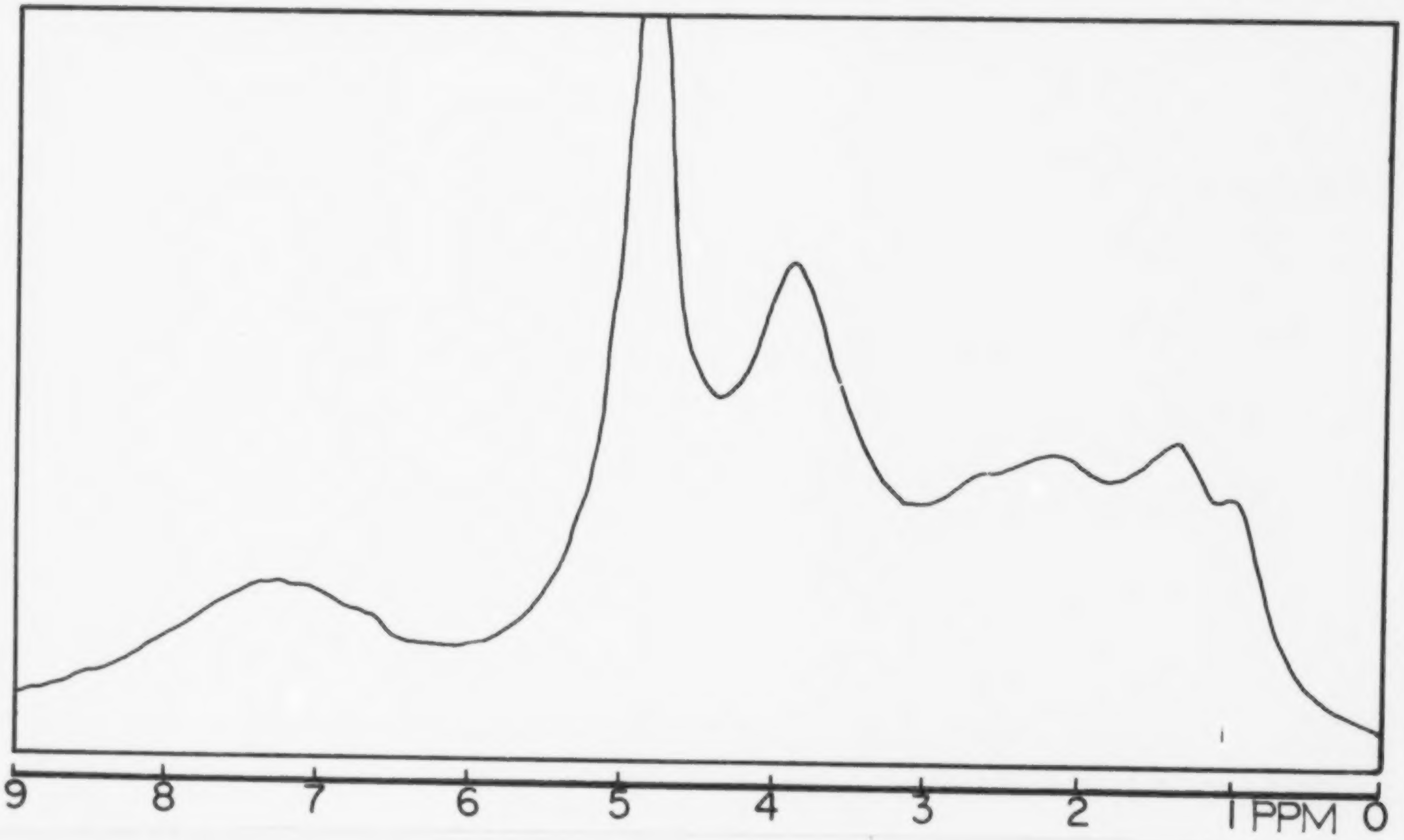

Figure 13. Proton NMR spectrum of Lake Drummond humic acid in 0.1 N NaOD/D$_2$O) 0.5-1.9 ppm, 22%; 1.9-3.1 ppm, 29%; 3.1-4.5 ppm, 30%; 6.0-9.0 ppm, 19%.

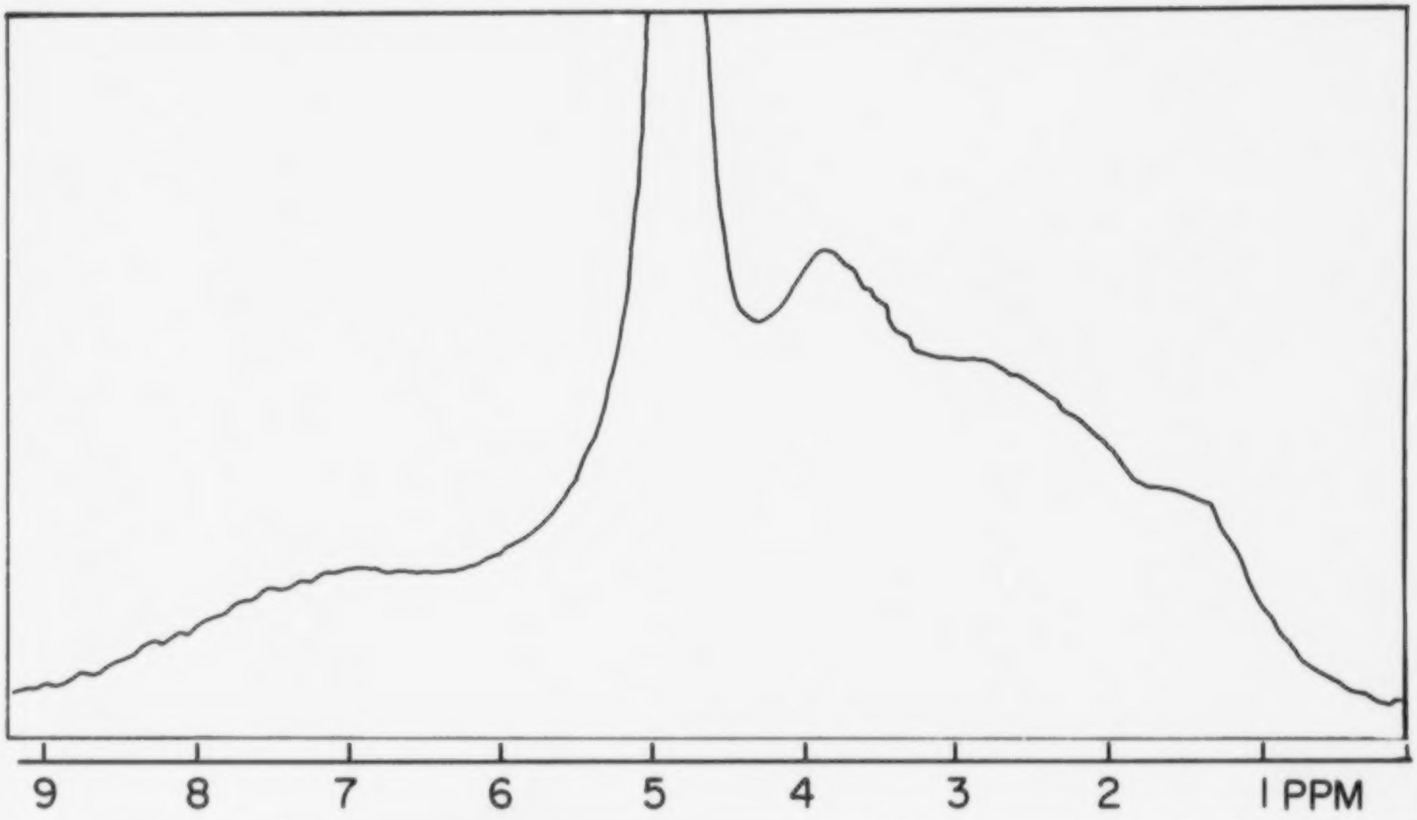

Figure 14. Proton NMR spectrum of Lake Drummond fulvic acid in D_2O.

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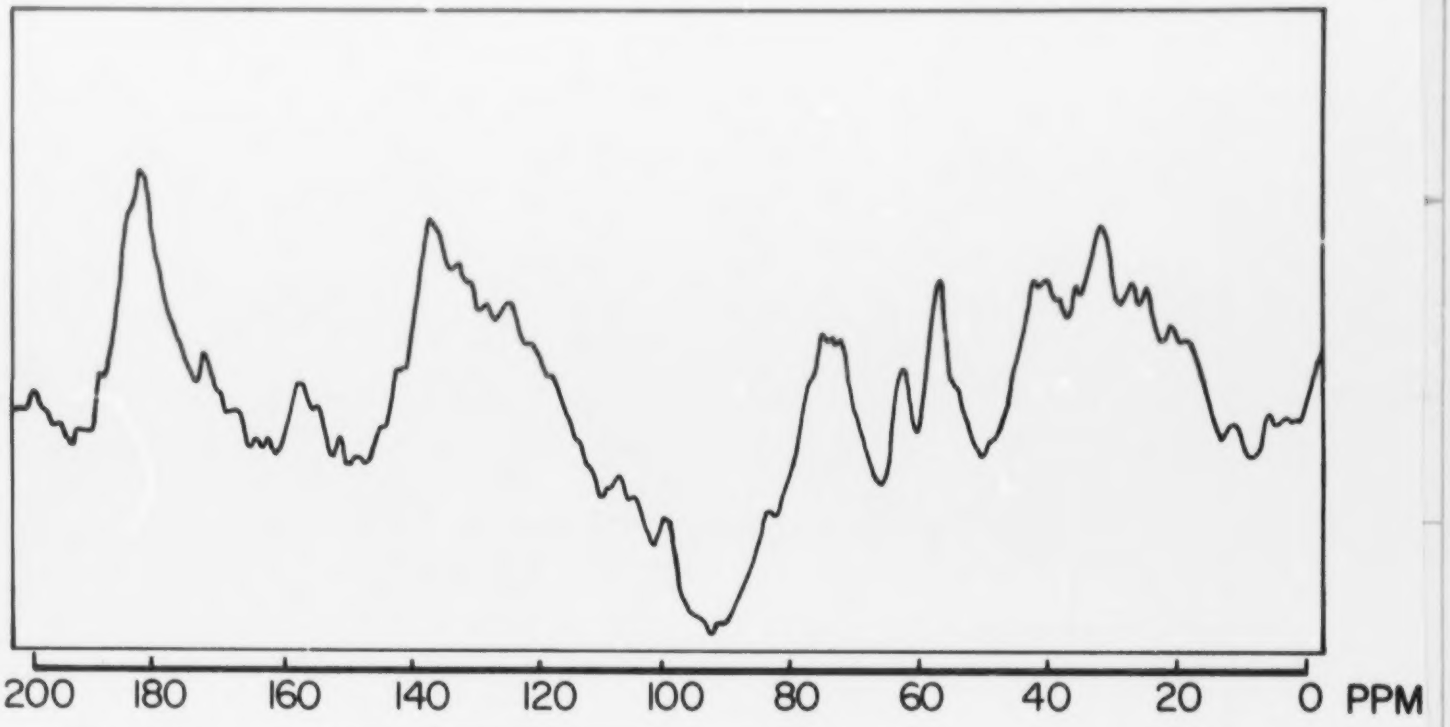

Figure 15. Proton-decoupled ^{13}C NMR spectrum of Lake Drummond humic acid in 0.1 N NaOD/D_2O.

20-45 ppm	Aliphatic carbon (~31%)
55-65 ppm	Carboxylate substituted aliphatic carbon (~7%)
70-80 ppm	Aliphatic alcohol, Ether (~7%)
115-135 ppm	Aromatic carbon (H, alkyl substituted, polyaromatic); Alkene (~27%)
150-156 ppm	Phenol, oxygen substituted aromatic (~3%)
170-185 ppm	Carbonyl carbon (~18%)
others	Undefined carbon (~7%)

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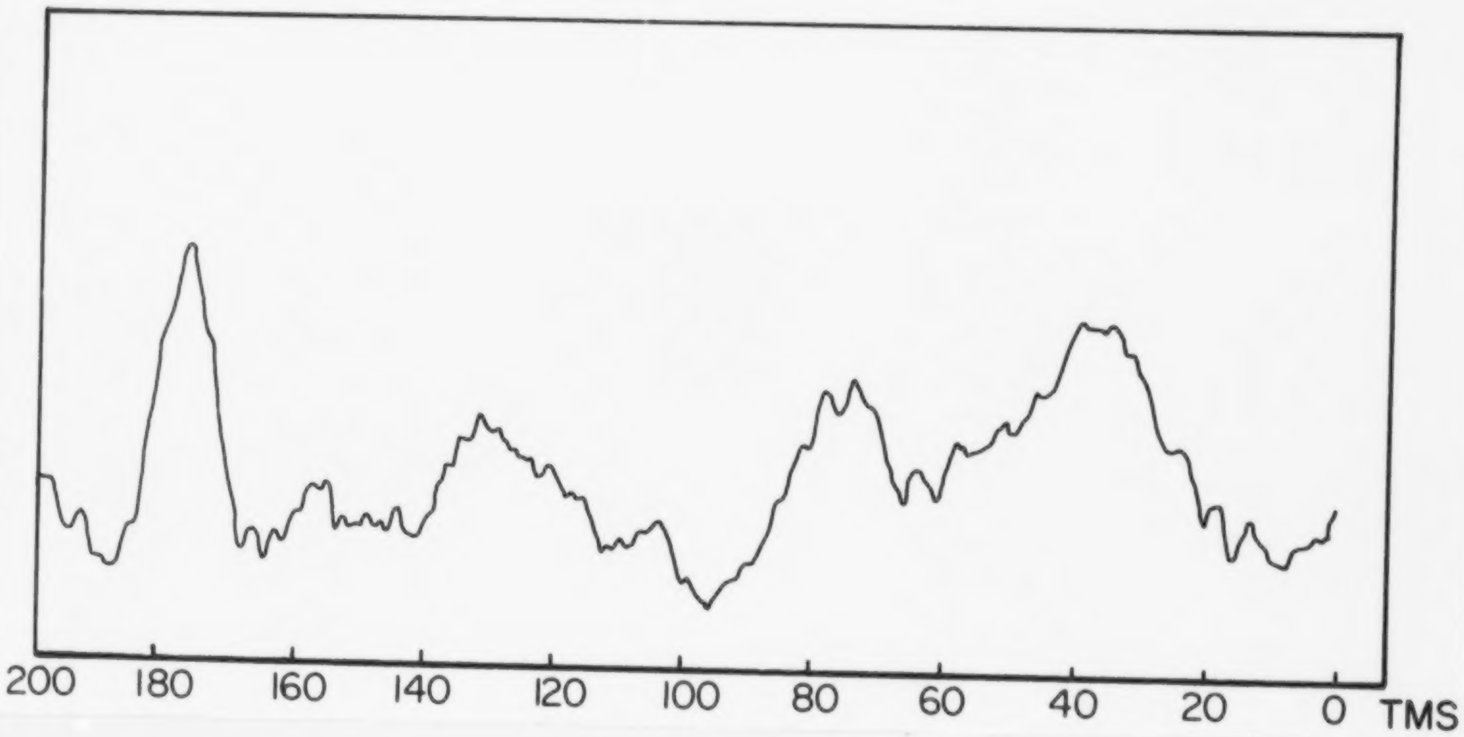

Figure 16. Proton-decoupled ^{13}C NMR spectrum of Lake Drummond fulvic acid in D_2O.

20-45 ppm Aliphatic carbon
55-65 ppm Carboxylate substituted aliphatic carbon
70-80 ppm Aliphatic alcohol, Ether
115-135 ppm Aromatic carbon (H, alkyl substituted; polyaromatic); Alkene
150-156 ppm Phenol, Oxygen substituted aromatic
170-185 ppm Carbonyl carbon.

HUMIC DEGRADATION EXPERIMENTS

With complex macromolecules such as humic materials, degradation is probably the most effective approach to obtain information on the aromatic components and the intermonomeric linkages present in their structures. There is sufficient experience with humic degradation experiments to state that the original humic macromolecule has both aromatic and aliphatic segments, and the aromatic-aliphatic hydrocarbon segments are partially oxidized and substituted by carboxyl, hydroxyl, and methoxy groups. It is reasonable to believe that the modes of intermonomeric linkage may include carbon to carbon bonds (alkyl-alkyl, alkyl-aryl, and aryl-aryl) as well as ether, ester, and hydrogen bond linkages. A few minor components including fatty acids, carbohydrates, phenolic compounds and nitrogen-derivatives are attached to the poly-aromatic-aliphatic segments through ester, ether, hydrogen bond, or carbon-carbon linkages. The significance of these hypothetic linkages is that different degradation procedures must be employed to break down the macromolecule into small fragments, to be followed by fractionation, extraction, purification, and GC/MS identification.

The degradation objectives of this research are summarized in Table 14. The methods used were selected based upon two criteria: first, the reaction of choice should be able to cleave humic materials into smaller pieces in significant yield, which can be identified by GC/MS, and it should not be too drastic. Second, the reaction should be specific such that the degraded fragments can be related to the original structures. Yields of the degradations were estimated by use of total organic carbon (TOC) measurements on aqueous samples and standard compounds for GC chromatographable materials.

TABLE 14. DEGRADATION OBJECTIVES

Procedure	Structural Effect
Alkaline Hydrolysis	Hydrolysis of ester and ether linkages
Alkaline $CuSO_4$ Oxidation	Oxidation of alkyl side chains and hydrolysis of ester and ether linkages
$KMnO_4$ Oxidation	Stronger oxidation of alkyl side chains
Alkaline Hydrolysis/$KMnO_4$ Oxidation	Hydrolysis of ester linkages followed by oxidation of alkyl side chains

Alkaline $CuSO_4$ Oxidation

A 2.5 g sample of the humic/hymatomelanic acid (HA) solid was dissolved in 50 mL of 5 N NaOH and stirred with heating. After addition of 2 g of $CuSO_4$ the mixture was refluxed for 40 hr. and cooled. Benzoic acid (25 mg) was added as an internal standard.

The degraded mixture was acidified with concentrated HCl to pH 1 filtered

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and extracted twice with 30 mL portions of ethyl acetate. The extracts were combined, dried over magnesium sulfate, and concentrated with N_2 to a volume of 2.5 mL.

GC-FID analyses of this extract using OV-17 and OV-101 on Chromosorb-W-AW (80/100 mesh, 6 ft. 1/8" OD, SS) did not show significant quantities of nonpolar products. However, formation of TMS derivatives with trimethyl silyldimethylamine at room temperature prior to GC/MS analysis resulted in the reconstructed gas chromatogram shown in Figure 17. Some of these products were identified by GC/MS and GC retention times on different columns with authentic models. Further confirmation was obtained with exact mass measurements and elemental compositions from high resolution mass spectra. The approximate yield of the degradation is 14% based upon the ratio of the ion intensity of the internal reference standard to the total ion intensity of all products separated on OV-101.

Alkaline Hydrolysis

Both HA and FA have been studied with base hydrolysis. The humic sample was refluxed for 1.5 hr. in 5 N NaOH, acidified to pH 2, centrifuged and the aqueous solution was extracted with ethyl acetate. The extract was dried over anhydrous Na_2SO_4 and concentrated under a nitrogen stream.

Both the methyl esters and the TMS derivatives of the extracted products were submitted to GC/MS analysis. The reconstructed gas chromatograms are shown in Figure 18 and Figure 19 in which product structural assignments have been made for several of the phenolic acids also appearing in the alkaline $CuSO_4$ products. Since these acids appear in the absence of oxidative conditions it is attractive to assume that they represent reactive groups bound via ester or ether linkages in the undegraded macromolecule.

$KMnO_4$ Oxidation of Un-Methylated Humic Substances

A 1 g sample of humic acid (HA) was suspended (or dissolved for FA) in 60 mL of water and the temperature of the mixture was maintained at 70-75°C. One g of $KMnO_4$ dissolved in an amount of water was added slowly to the mixture over a period of 1 hr. The mixture was then made basic with 5 mL of 5 N NaOH solution to dissolve the remaining humic particulates. One g of $KMnO_4$ in water was added, and the reaction was allowed to proceed for another hour. No excess permagnate was found at the end point. The reaction mixture was filtered, and the filtrate was acidified with conc. HCl and extracted with ether and ethyl acetate.

The combined extracted products in organic solvent were methylated with diazomethane and submitted to GC/MS analysis. The result is shown in Figure 20. Figure 21 also shows the reconstructed gas chromatogram (RGC) for the TMS derivatized sample. The GC/MS result of the oxidation of FA is shown in Figure 22.

The acidic aqueous solution which had previously been extracted with ether and ethyl acetate was freeze dried and extracted with a solution

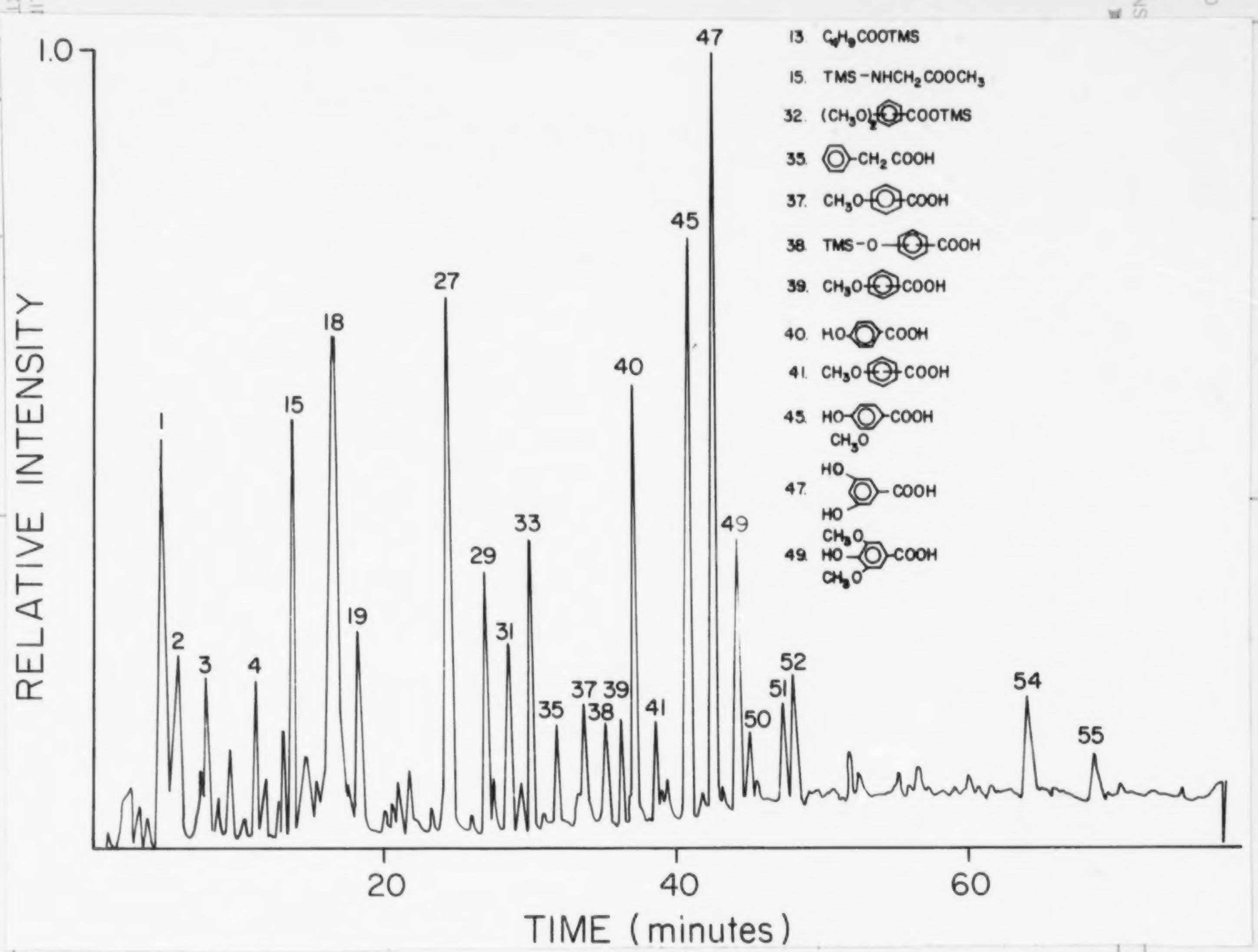

Figure 17. Alkaline CuSO4 degradation products of aquatic humic acid.

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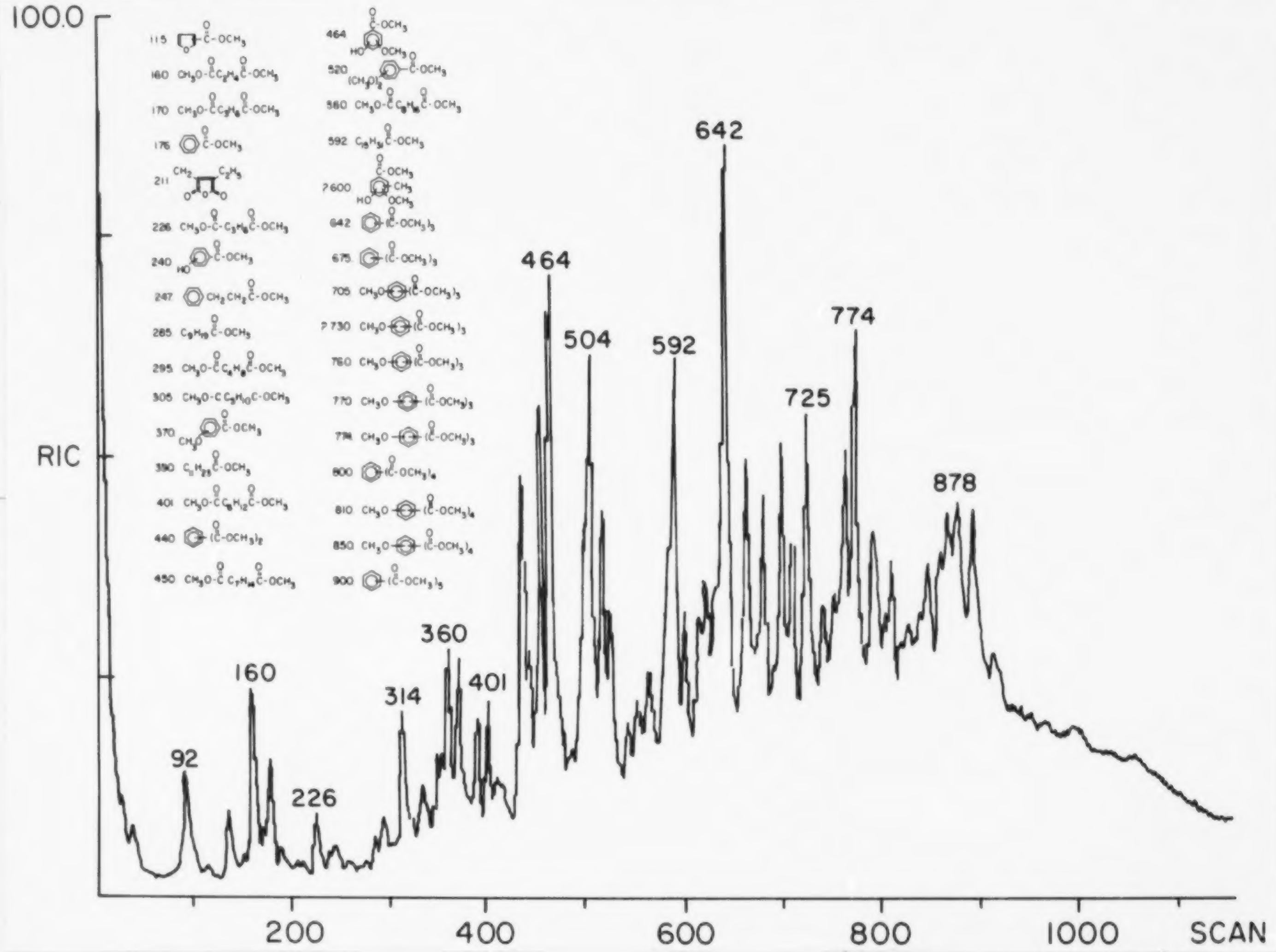

Figure 18. NaOH hydrolysis products (methyl ester) of aquatic humic acid.

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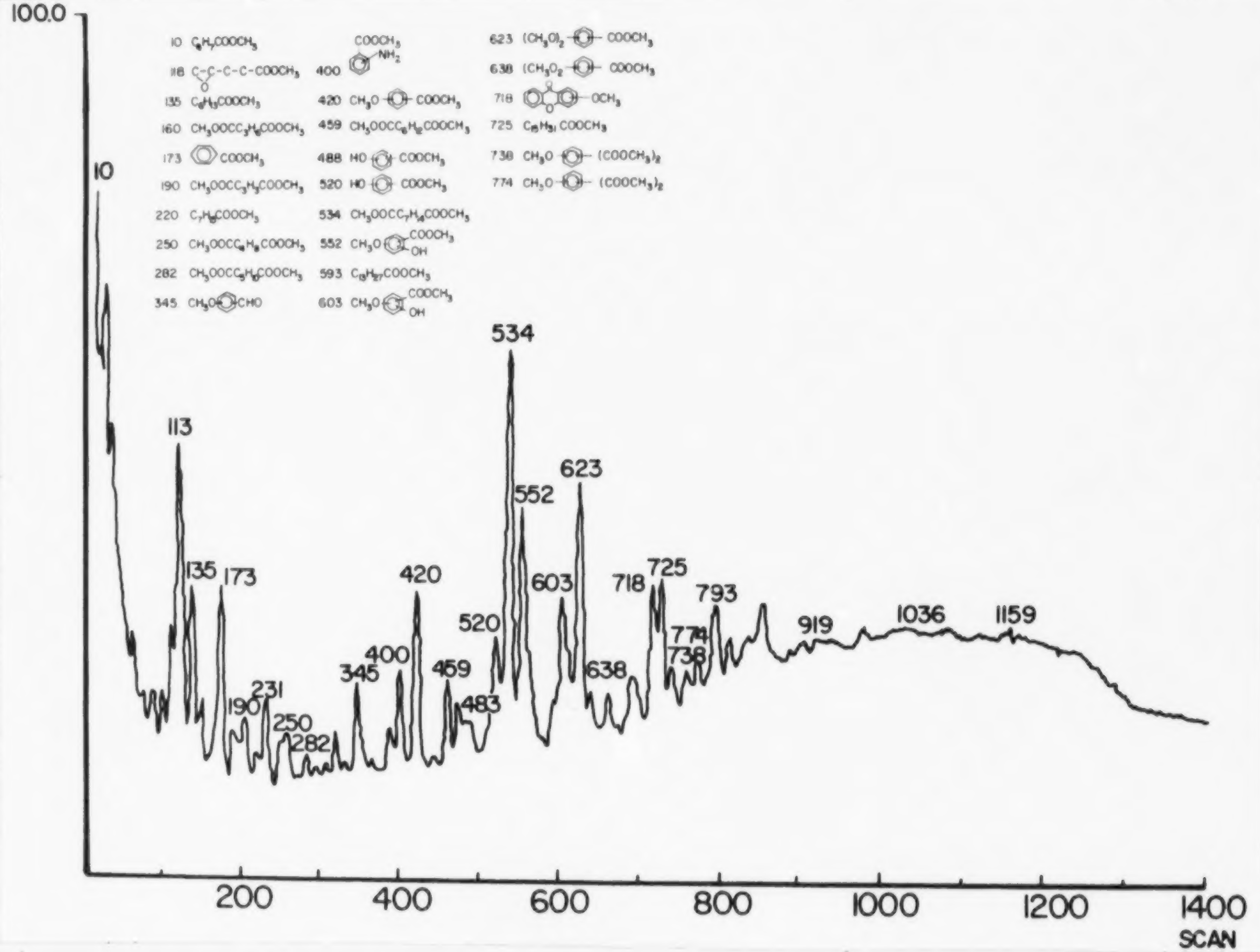

Figure 19. NaOH hydrolysis products (methyl ester) of aquatic fulvic acid.

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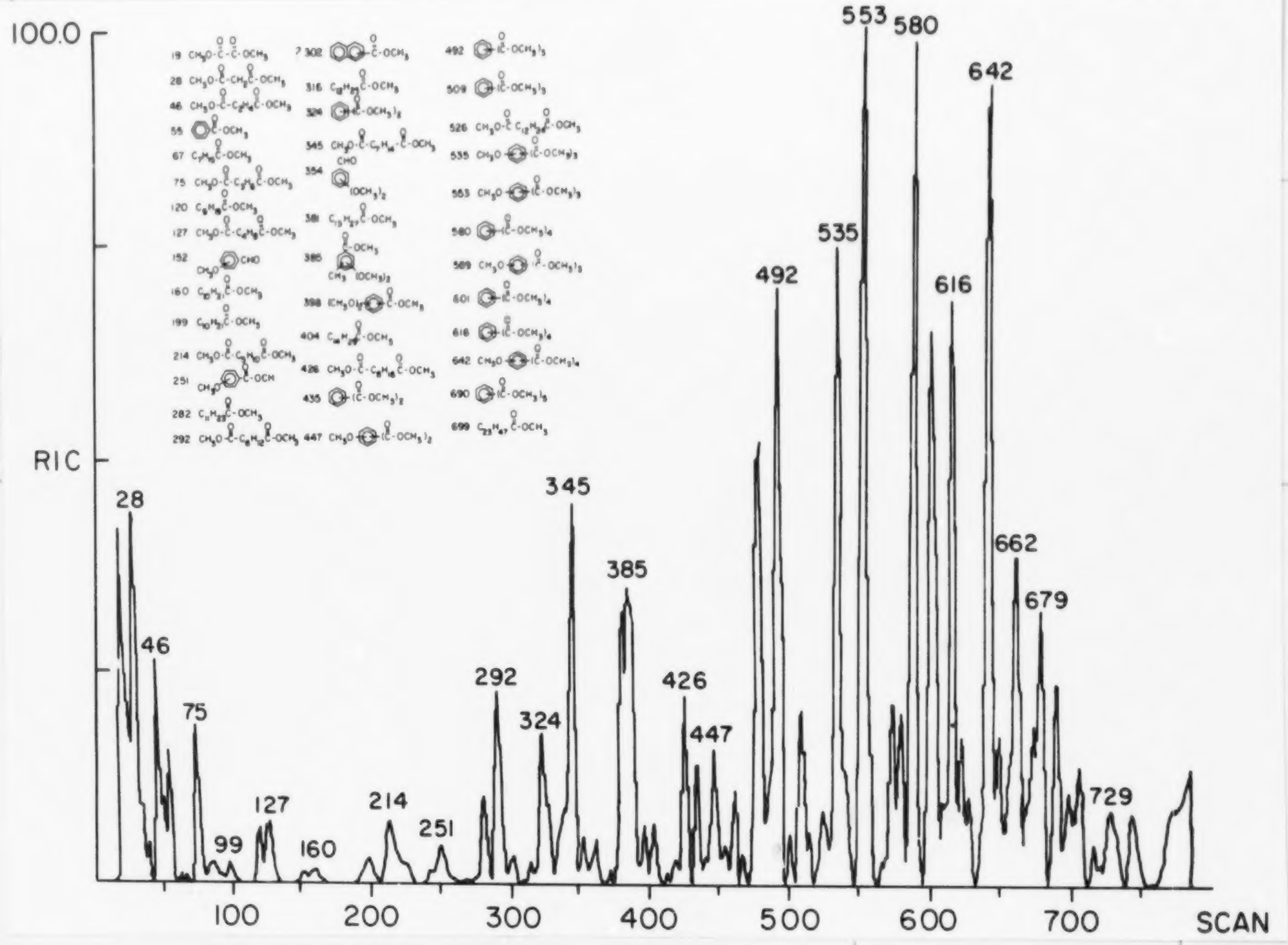

Figure 20. $KMnO_4$ degradation products (methyl ester) of aquatic humic acid.

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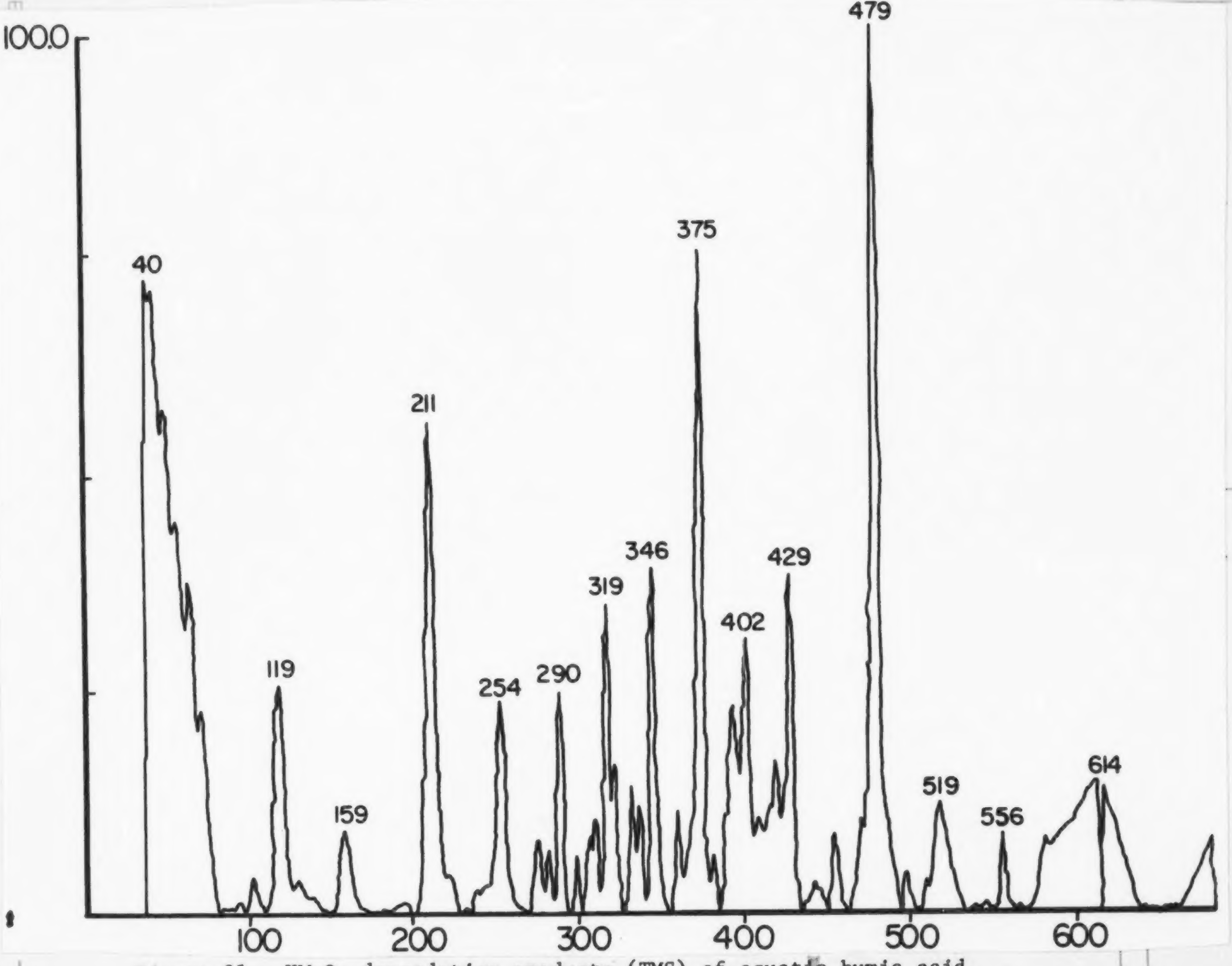

Figure 21. $KMnO_4$ degradation products (TMS) of aquatic humic acid.

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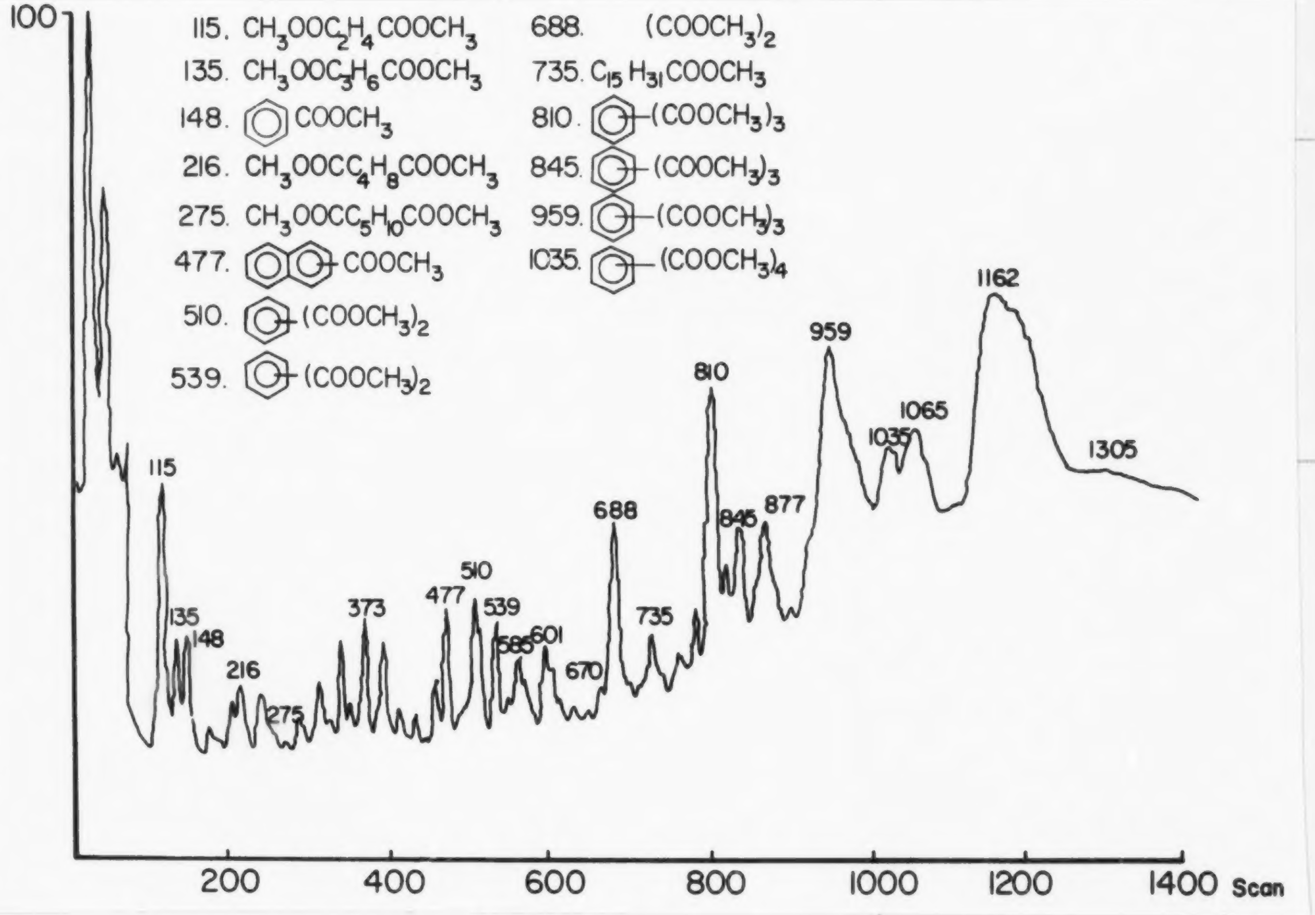

Figure 22. $KMnO_4$ degradation products (methyl ester) of aquatic fulvic acid.

of diazomethane in ethyl acetate. The methylated and extracted products were analyzed with GC/MS. The results are shown in Figure 23.

The distribution of degraded humic fragments during the permanganate oxidation procedures was determined by measuring the organic carbon contents with a Dohrmann DC-54 total organic carbon analyzer. These data indicate that 14% of the total organic carbon (TOC) submitted to degradation reaction was lost in the permanganate oxidation by conversion to carbon dioxide or other volatile molecules. Twenty-nine percent of the original TOC was extracted into the organic fraction in which 41% out of the 29% TOC was gas chromatographable on OV-17 (temperature up to 285°C). The aqueous fraction that has been extracted with organic solvents still retained 49% of the TOC. This fraction was freeze dried and extracted with solution of diazomethane in ethyl acetate. The amount of the extracted products was estimated by measuring standardized peak areas on a gas chromatograph. The total GC peak area displayed on OV-17 accounts for approximately 21% of the degraded humic fragments in this fraction. Some humic residues were firmly adsorbed onto the manganese dioxide solid. The degree of adsorption was estimated by measuring the TOC before and after filtration. The difference between these two values indicated that the adsorbed residues account for 9% of the TOC.

NaOH Hydrolysis/$KMnO_4$ Oxidation

The humic residue, which had previously been hydrolyzed in 5 N NaOH and washed thoroughly with ethyl acetate and dried in vacuum, was subjected to oxidation with permanganate. The sample was worked up by the same procedures as described above.

The extracted products were methylated with diazomethane. The results of the GC/MS analysis are shown in Figure 24.

$KMnO_4$ Oxidation of Methylated Humic Substances

Two methods have been employed to prepare methyl esters of the humic acid fraction for our degradation studies. The first followed the procedure of Wershaw and Pinckney (3). The humic acid sample was methylated with diazomethane, dimethyl sulfate. and methyl iodide in a three-step procedure. In the second method, humic acid was exhaustively methylated with excess diazomethane in ethyl acetate. Both samples of methylated humic acid (MHA) were examined in permanganate oxidation studies. The degradation experiments of the methylated humic acid samples were carried out in the same way as was described above except 1 g of methylated sample was oxidized with 3 g of $KMnO_4$. The GC/MS analysis of the extracted degradation products is shown in Figure 25 and Table 15. The yield estimated by measuring standardized GC area was about 24.5% of the original total organic carbon.

H_5IO_6 Oxidation

A 0.5 g sample of humic acid (HA) was suspended in 20 ml of water with stirring. An excess amount of (1 g) of paraperiodic acid was added to the mixture. The reaction was kept at room temperature for 36 hr. The mixture was transferred to a dialysis bag and dialyzed against deionized distilled

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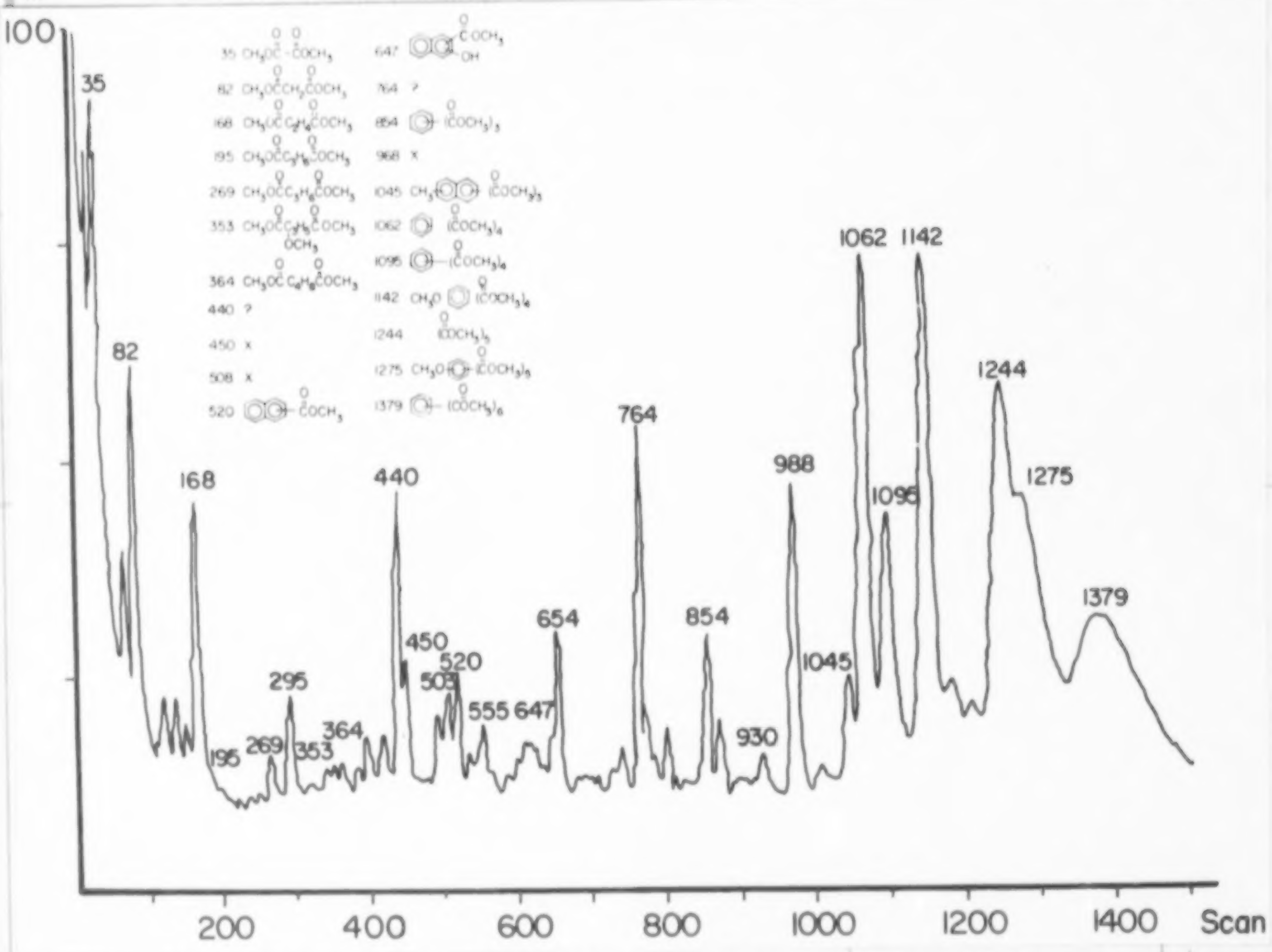

Figure 23. $KMnO_4$ degradation products (aqueous residues, methyl ester) of aquatic humic acid.

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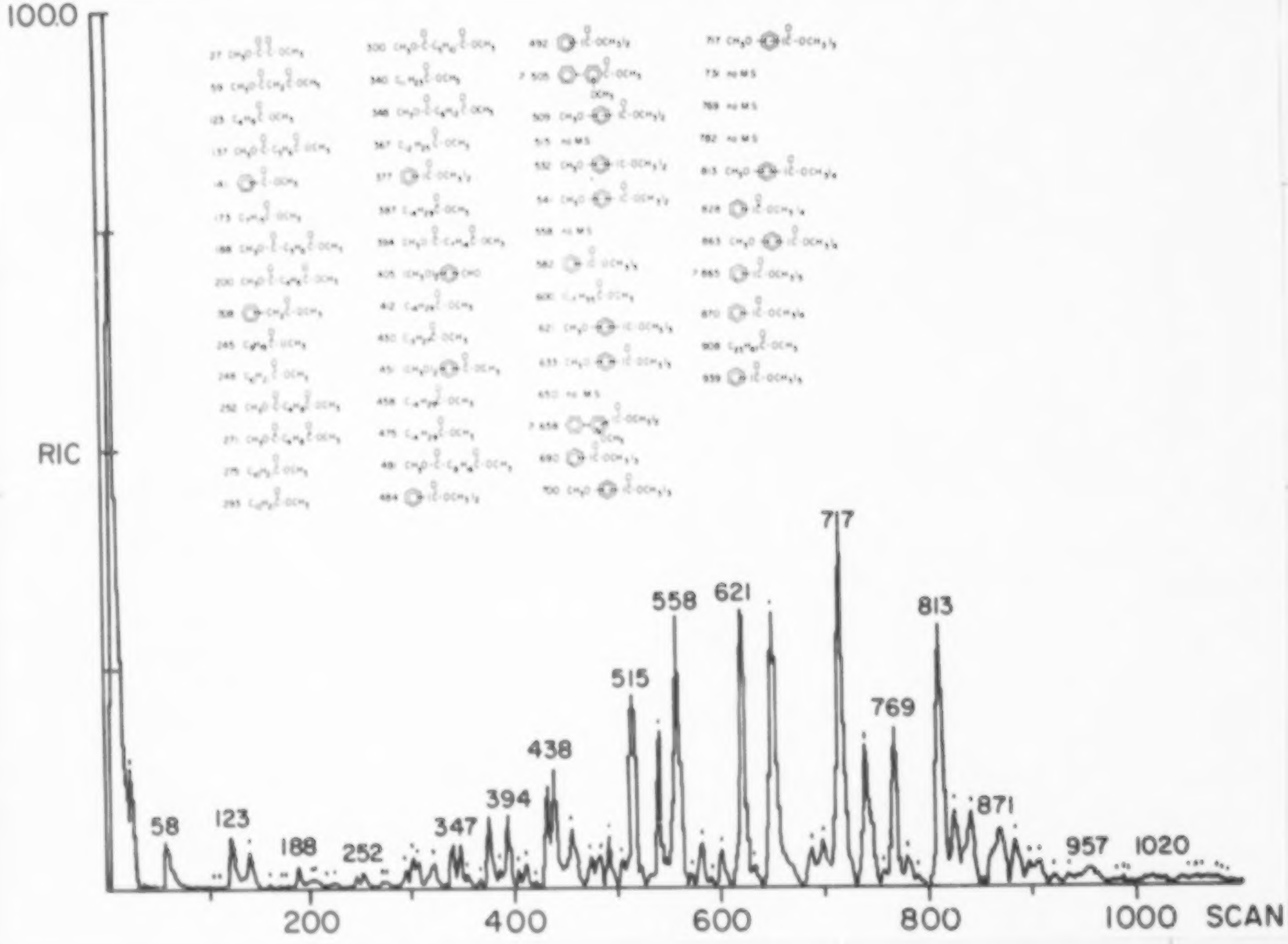

Figure 24. NaOH/KMnO$_4$ degradation products (methyl ester) of aquatic humic acid.

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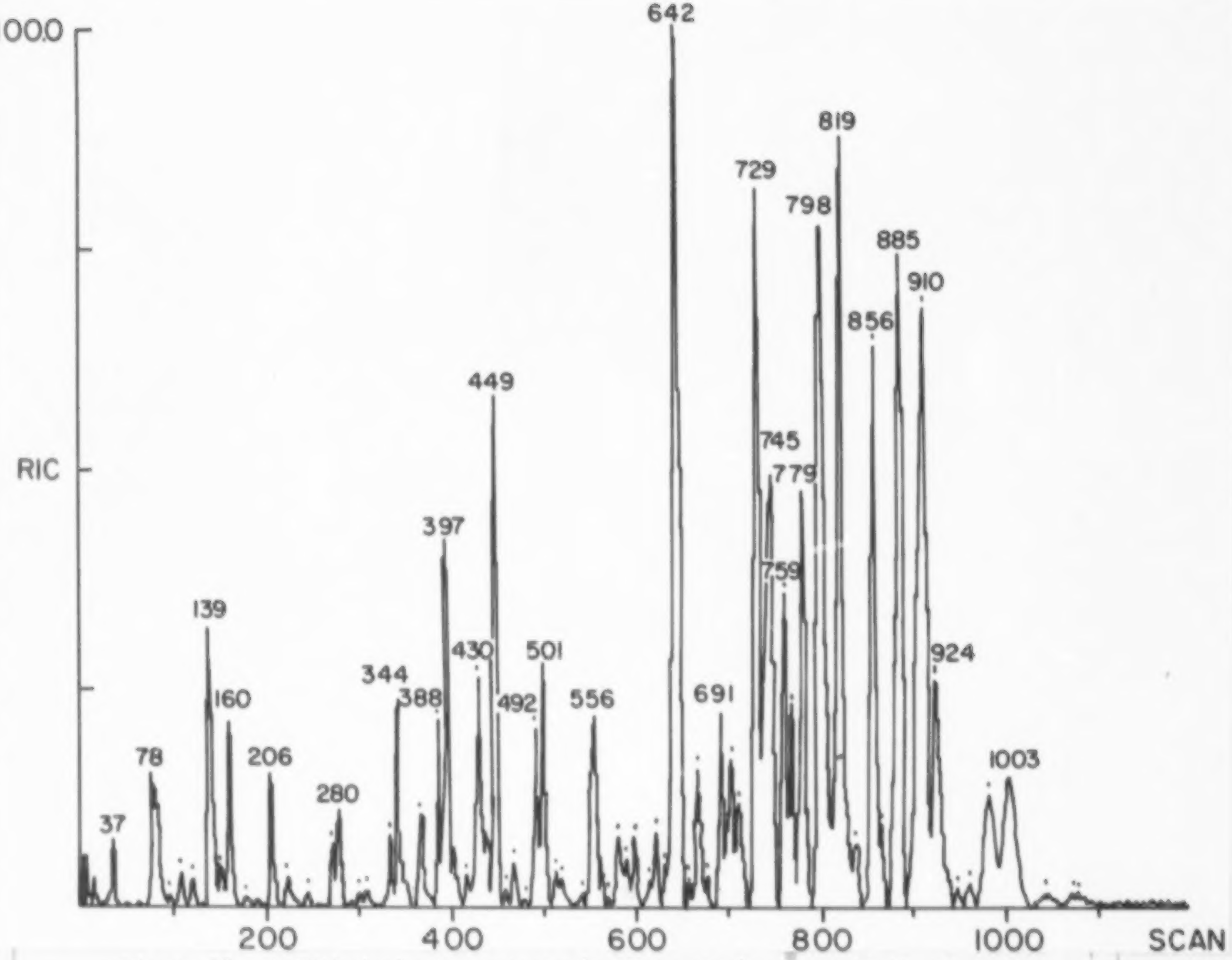

Figure 25. NaOH hydrolysis products (methyl ester) of aquatic humic acid.

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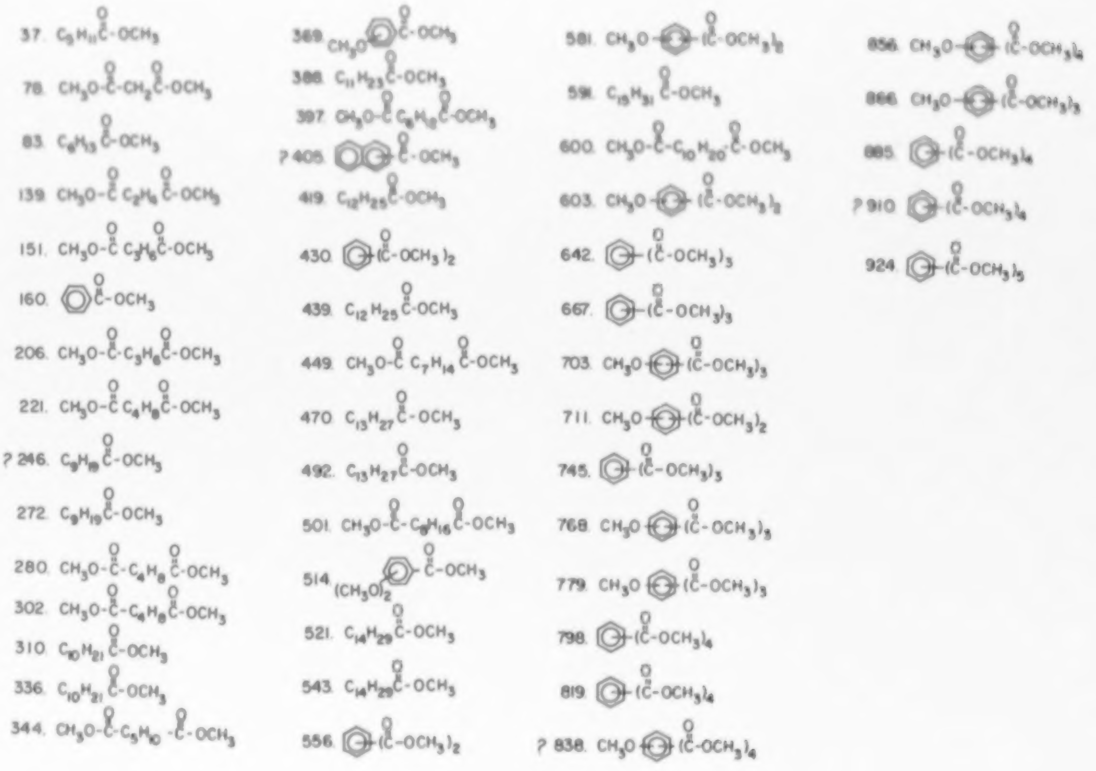
TABLE 15. PERMANGANATE OXIDATION PRODUCTS (METHYL ESTER) OF METHYLATED HUMIC ACID


37. $C_5H_{11}\overset{O}{\overset{\|}{C}}-OCH_3$
78. $CH_3O-\overset{O}{\overset{\|}{C}}-CH_2\overset{O}{\overset{\|}{C}}-OCH_3$
83. $C_6H_{13}\overset{O}{\overset{\|}{C}}-OCH_3$
139. $CH_3O-\overset{O}{\overset{\|}{C}}\ C_2H_4\overset{O}{\overset{\|}{C}}-OCH_3$
151. $CH_3O-\overset{O}{\overset{\|}{C}}\ C_3H_6\overset{O}{\overset{\|}{C}}-OCH_3$
160. $\overset{O}{\overset{\|}{C}}-OCH_3$
206. $CH_3O-\overset{O}{\overset{\|}{C}}-C_3H_6\overset{O}{\overset{\|}{C}}-OCH_3$
221. $CH_3O-\overset{O}{\overset{\|}{C}}\ C_4H_8\overset{O}{\overset{\|}{C}}-OCH_3$
? 246. $C_9H_{18}\overset{O}{\overset{\|}{C}}-OCH_3$
272. $C_9H_{19}\overset{O}{\overset{\|}{C}}-OCH_3$
280. $CH_3O-\overset{O}{\overset{\|}{C}}-C_4H_8\overset{O}{\overset{\|}{C}}-OCH_3$
302. $CH_3O-\overset{O}{\overset{\|}{C}}-C_4H_8\overset{O}{\overset{\|}{C}}-OCH_3$
310. $C_{10}H_{21}\overset{O}{\overset{\|}{C}}-OCH_3$
336. $C_{10}H_{21}\overset{O}{\overset{\|}{C}}-OCH_3$
344. $CH_3O-\overset{O}{\overset{\|}{C}}-C_5H_{10}-\overset{O}{\overset{\|}{C}}-OCH_3$
369. CH_3O $\overset{O}{\overset{\|}{C}}-OCH_3$
388. $C_{11}H_{23}\overset{O}{\overset{\|}{C}}-OCH_3$
397. $CH_3O-\overset{O}{\overset{\|}{C}}\ C_8H_{16}\overset{O}{\overset{\|}{C}}-OCH_3$
? 405. $\overset{O}{\overset{\|}{C}}-OCH_3$
419. $C_{12}H_{25}\overset{O}{\overset{\|}{C}}-OCH_3$
430. $(\overset{O}{\overset{\|}{C}}-OCH_3)_2$
439. $C_{12}H_{25}\overset{O}{\overset{\|}{C}}-OCH_3$
449. $CH_3O-\overset{O}{\overset{\|}{C}}\ C_7H_{14}\overset{O}{\overset{\|}{C}}-OCH_3$
470. $C_{13}H_{27}\overset{O}{\overset{\|}{C}}-OCH_3$
492. $C_{13}H_{27}\overset{O}{\overset{\|}{C}}-OCH_3$
501. $CH_3O-\overset{O}{\overset{\|}{C}}-C_8H_{16}\overset{O}{\overset{\|}{C}}-OCH_3$
514. $(CH_3O)_2$ $\overset{O}{\overset{\|}{C}}-OCH_3$
521. $C_{14}H_{29}\overset{O}{\overset{\|}{C}}-OCH_3$
543. $C_{14}H_{29}\overset{O}{\overset{\|}{C}}-OCH_3$
556. $(\overset{O}{\overset{\|}{C}}-OCH_3)_2$
581. CH_3O- $(\overset{O}{\overset{\|}{C}}-OCH_3)_2$
591. $C_{15}H_{31}\overset{O}{\overset{\|}{C}}-OCH_3$
600. $CH_3O-\overset{O}{\overset{\|}{C}}-C_{10}H_{20}-\overset{O}{\overset{\|}{C}}-OCH_3$
603. CH_3O $(\overset{O}{\overset{\|}{C}}-OCH_3)_2$
642. $(\overset{O}{\overset{\|}{C}}-OCH_3)_3$
667. $(\overset{O}{\overset{\|}{C}}-OCH_3)_3$
703. CH_3O $(\overset{O}{\overset{\|}{C}}-OCH_3)_3$
711. CH_3O $(\overset{O}{\overset{\|}{C}}-OCH_3)_2$
745. $(\overset{O}{\overset{\|}{C}}-OCH_3)_3$
768. CH_3O $(\overset{O}{\overset{\|}{C}}-OCH_3)_3$
779. CH_3O $(\overset{O}{\overset{\|}{C}}-OCH_3)_3$
798. $(\overset{O}{\overset{\|}{C}}-OCH_3)_4$
819. $(\overset{O}{\overset{\|}{C}}-OCH_3)_4$
? 838. CH_3O $(\overset{O}{\overset{\|}{C}}-OCH_3)_4$
856. CH_3O- $(\overset{O}{\overset{\|}{C}}-OCH_3)_4$
866. CH_3O- $(\overset{O}{\overset{\|}{C}}-OCH_3)_3$
885. $(\overset{O}{\overset{\|}{C}}-OCH_3)_4$
? 910. $(\overset{O}{\overset{\|}{C}}-OCH_3)_4$
924. $(\overset{O}{\overset{\|}{C}}-OCH_3)_5$

water for 2 days and then freeze dried in a vacuum.

Both humic samples before and after H_5IO_6 oxidation were dissolved in 0.1 N NaOD solution and submitted to NMR analysis. The spectra (Figure 26) show that the resonances in the 2.4-4.4 ppm region which are characeristic of protons on carbon substituted by an oxygen atom(s) almost disappear after H_5IO_6 oxidation.

RESULTS

The data in Figures 17-25 suggest that methylation is a preferable derivatization technique compared to trimethyl silylation. Many of the same humic degradation products are found by use of both derivatization techniques, with the exception that the hydroxy-, and hydroxy-methoxy cinnamic acid degradation products appear in the TMS teated sodium hydroxide hydrolysis mixtures. In general the separations obtained with the methyl esters formed from diazomethane treatment are better.

It is important to emphasize that the data displayed in Figures 17-25 are not the result of individual experiments. Rather, these reconstructed gas chromatograms and the compounds identified in them are reproducible from one experiment to the next. Examination of the structural identifications attached to each figure reveals that four different categories of degradation products are present after these degradation procedures. These are monobasic aliphatic acids, dibasic aliphatic acids, mono- and polybasic aromatic acids, and miscellaneous aromatic products (aldehydes, biphenyl and naphthylinic derivatives), and substituted furans. The numbers of compounds identified from these degradation experiments constitute the largest amount of structural information regarding aquatic humic acids that is available.

The data in Tables 16, 17, and 18 establish that the aromatic and heterocyclic degradation products are the dominant materials produced from these degradation procedures, accounting for approximately 50 to over 70% of the total GC peak areas displayed. The monobasic acid aliphatic products account for as little as 2 to 13%, and the dibasic acid aliphatic products account from 5 to over 17%. The total identification effort of all degradation products is quite good ranging from slightly under 70% for the sodium hydroxide hydrolysis to over 90% for the permanganate degradation experiments.

The yields of each of the degradation experiments indicated in Tables 16, 17 and 18 have been estimated by the use of a standard solution of 1, 2, 4-benzene tricarboxylic acid. This standard was chosen because of the dominance of this type of structure in the degradation mixture. By injecting a known concentration of the standard and measuring the peak area produced, assuming a constant response per unit of carbon, total concentrations of organic carbon represented by the RGC peak area were calculated. The percentage of the total RGC peak area represented by each identified product was then determined, and a sub-total, representing the percentage of total peak area of each product category was calculated by suming the individual percentages. Yields are the percent of original humic carbon

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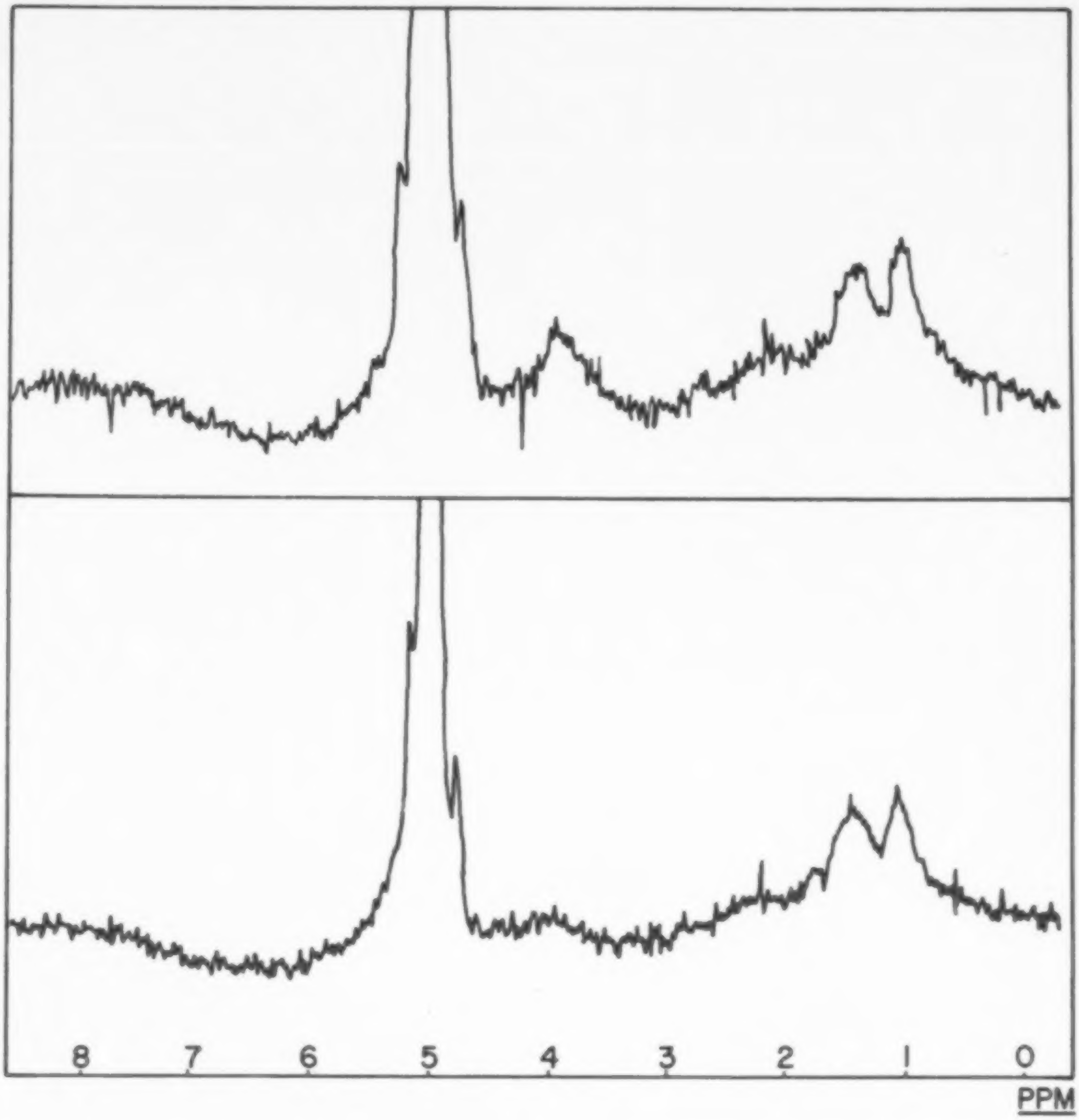

Figure 26. ^{1}H NMR spectra of Black Lake humic acid (HA) in 0.1 N NaOH before (above) and after (below) H_5IO_6 oxidation.

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TABLE 16. AROMATIC DEGRADATION PRODUCTS

Relative Abundance (% Total GC Peak Area)

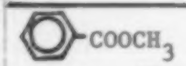
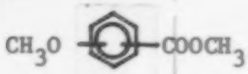
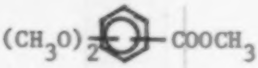
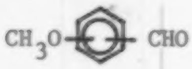
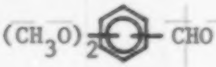
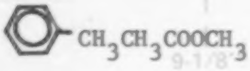
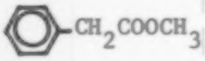
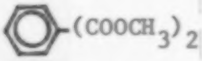
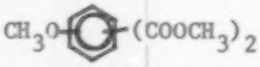
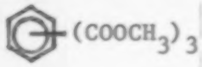
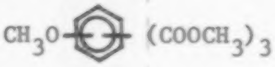
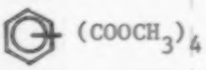
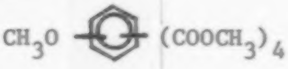
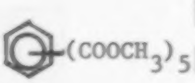
Compound \ Degradation	HA KMnO$_4$	HA NaOH	HA CuSO$_4$	FA KMnO$_4$	FA NaOH	HA NaOH/ KMnO$_4$	MHA KMnO$_4$
	0.4	1.0	-	-	a	0.7	1.8
	0.3	1.8	a	-	a	-	0.7
	1.1	1.6	a	-	a	0.02	0.1
	0.1	-	-	-	a	0.02	-
	0.3	-	-	-	-	0.1	-
	-	0.2	-	-	-	-	-
	-	-	a	-	-	0.1	-
	2.0	5.6	-	a	-	2.5	5.1
	4.0	-	-	-	a	3.6	0.7
	7.7	11.5	-	a	-	11.5	26.0
	15.2	15.1	-	a	-	32.1	1.0
	13.0	2.5	-	a	-	2.6	31.0
	8.9	1.6	-	-	-	8.9	4.2
	3.2	2.4	-	-	-	0.3	1.9

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TABLE 16 (continued)

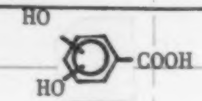
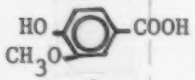
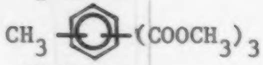
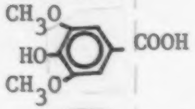
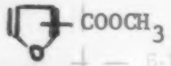
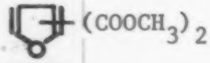
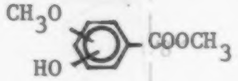
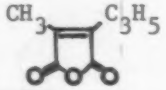
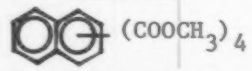
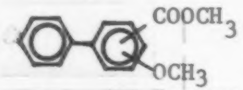
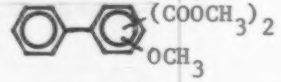
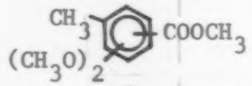
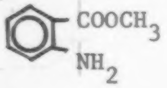
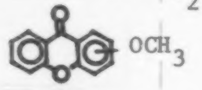
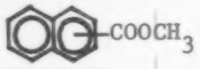
Compound \ Degradation	HA KMnO$_4$	HA NaOH	HA CuSO$_4$	FA KMnO$_4$	FA NaOH	HA NaOH/ KMnO$_4$	MHA KMnC$_4$
	–	–	a	–	–	–	–
 HO CH$_3$O COOH	–	–	a	–	–	–	–
 CH$_3$ (COOCH$_3$)$_3$	–	–	–	–	–	–	–
 CH$_3$O HO CH$_3$O COOH	–	–	a	–	–	–	–
	–	0.2	–	–	–	–	–
	–	–	–	–	–	–	0.01
 CH$_3$O HO COOCH$_3$	–	5.9	–	–	–	–	–
	–	0.2	–	–	–	–	–
	0.3	–	–	–	–	–	–
 COOCH$_3$ OCH$_3$	–	0.1	–	–	–	–	–
 (COOCH$_3$)$_2$ OCH$_3$	–	0.1	–	–	–	–	–
 CH$_3$ (CH$_3$O)$_2$ COOCH$_3$	2.9	–	–	–	–	–	–
	–	–	–	–	a	–	–
	–	–	–	–	a	–	–
	0.4	–	a	–	–	–	–

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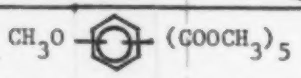
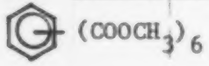
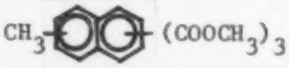
TABLE 16 (continued)

Compound \ Degradation	HA $KMnO_4$	HA NaOH	HA $CuSO_4$	FA $KMnO_4$	FA NaOH	HA NaOH/ $KMnO_4$	MHA $KMnC_4$
 CH_3O $(COOCH_3)_5$	1.1	-	-	-	-	-	-
 $(COOCH_3)_6$	5.0	-	-	-	-	-	-
 CH_3 $(COOCH_3)_3$	0.6	0.01	-	-	-	-	-
Sub-Total (% of RGC)	66.5	51.8				62.4	72.5
Yield (Total RGC as % of Starting Carbon)	20.9	3.0	14.0			11.4	24.5

a Compound present but yield data not available.

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TABLE 17. DIBASIC ACIDS-ALIPHATIC PRODUCTS

Degradation / Compound	(% Total RGC Peak Area) HA $KMnO_4$	HA $NaOH$	HA $CuSO_4$	FA $KMnO_4$	FA $NaOH$	HA $NaOH/KMnO_4$	MHA $KmnO_4$
$CH_3OOC-COOCH_3$	2.9	-	-	-	-	0.7	-
$CH_3OOCCH_2COOCH_3$	5.5	-	-	-	-	1.2	1.4
$CH_3OOCC_2H_4COOCH_3$	3.4	2.8	-	a	-	-	2.9
$CH_3OOCC_3H_6COOCH_3$	1.6	1.5	-	a	a	0.3	1.4
$CH_3OOCC_4H_8COOCH_3$	0.7	1.4	-	a	a	0.2	0.7
$CH_3OOCC_5H_{10}COOCH_3$	0.4	0.7	-	a	a	0.3	1.1
$CH_3OOCC_6H_{12}COOCH_3$	1.0	1.0	-	-	a	0.6	3.6
$CH_3OOCC_7H_{14}COOCH_3$	2.3	3.6	-	-	a	1.6	5.1
$CH_3OOCC_8H_{16}COOCH_3$	0.8	0.6	-	-	-	0.3	-
$CH_3OOCC_9H_{18}COOCH_3$	-	-	-	-	-	-	-
$CH_3OOCC_{10}H_{20}COOCH_3$	0.4	-	-	-	-	-	-
$CH_3OOCC_{11}H_{22}COOCH_3$	-	-	-	-	-	-	-
$CH_3OOCC_{12}H_{24}COOCH_3$	0.2	-	-	-	-	-	0.4
Sub-Total (% of RGC)	19.2	10.6				5.2	16.6
Yield (Total RGC as % of Staring Carbon)	20.9	3.0	14.0			11.4	24.5

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TABLE 18. MONOBASIC ACIDS-ALIPHATIC PRODUCTS

Degradation / Compound	(% Total RGC Peak Area) HA $KMnO_4$	HA NaOH	HA $CuSO_4$	FA $KMnO_4$	FA NaOH	HA NaOH/ $KMnO_4$	MHA $KMnO_4$
$C_4H_7COOCH_3$	-	-	a	-	a	-	-
$C_4H_9COOCH_3$	-	-	-	-	-	1.3	0.2
$NH_2CH_2COOCH_3$	-	-	a	-	-	-	-
$C_6H_{13}COOCH_3$	-	-	-	-	a	-	-
$C_7H_{15}COOCH_3$	0.02	-	-	-	a	0.06	-
$C_9H_{19}COOCH_3$	0.2	0.3	-	-	-	0.06	-
$C_{10}H_{21}COOCH_3$	0.2	-	-	-	-	0.4	0.07
$C_{11}H_{23}COOCH_3$	0.4	0.8	-	-	-	0.5	0.9
$C_{12}H_{25}COOCH_3$	0.05	-	-	-	-	0.1	0.2
$C_{13}H_{27}COOCH_3$	0.8	-	-	-	a	2.5	0.4
$C_{14}H_{29}COOCH_3$	0.4	-	-	-	-	2.1	0.1
$C_{15}H_{31}COOCH_3$	0.06	5.6	-	a	a	4.6	0.1
$C_{17}H_{35}COOCH_3$	-	-	-	-	-	1.2	-
$C_{23}H_{47}COOCH_3$	0.2	-	-	-	-	0.2	-
$\underset{O}{C-C}\ CH_2CH_2COOCH_3$	0.6	-	-	-	a	-	-
Sub-Total (% of RGC)	2.4	6.7				13.0	2.1
Yield (Total RGC as % of Starting Carbon)	20.9	3.0	14.0			11.4	24.5

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represented by the total RGC peak area. Inspection of the yield data at the bottom of Table 16 indicates that the greatest yields were obtained from permanganate oxidation of both the methylated and unmethylated humic acids. Prior hydrolysis by sodium hydroxide apparently decreases the subsequent yield from permanganate oxidation although the $KMnO_4$ oxidation of methylated humic acids results in greater yields than $KMnO_4$ oxidation of unmethylated humic acids.

Inspection of the relative abundance data in Tables 16, 17, and 18 reveals that the dominant degradation product in all cases is a benzene tricarboxylic acid, with the exception of the permanganate oxidation of methylated humic acids in which the dominant product is the benzene tetracarboxylic acid. These degradation procedures apparently do not produce alkyl side chains of more than one carbon length in any appreciable quantities as two and three carbon side chains were found only as trace constituents. No particular pattern of odd versus even carbon chain length is apparent in the mono-basic acid aliphatic product identification list. The absence of compounds below C_4 is not conclusive as they may have been missed with the gas chromatographic procedures employed. Similarly a complete homologous series of dibasic acids from oxalic through the C_{12} dibasic acid is apparent from the data in Table 17.

Some molecules are lost in the permanganate oxidation by conversion to carbon dioxide or other extremely volatile products. The degree of this loss (Figure 27) was estimated by measuring the total organic carbon concentrations after permanganate oxidation and prior to ethyl acetate extraction for GC/MS analysis. Although both the Wershaw methylation procedure and excess diazomethane methylation procedure were studied, the Wershaw procedure has been abandoned because of evidence of formation of sulfur-containing products of reaction of dimethylsulfate with the humic materials, products resulting from reactions other than the desired methylations.

DISCUSSION

If the sodium hydroxide hydrolysis is serving the function of cleaving ester and ether linkages in the humic macromolecule, then a knolwedge of the degradation products shown in Tables 16-18 indicates that:

- esters are more important structural features than ethers in the macromolecule because no alcoholic products were found. A possible exception, of course, would be aromatic esters.
- the type of esters dominant in the humic macromolecule are aliphatic acid-O-aromatic and not aliphatic-O-aromatic acid, again because of the absence of alcohols in these degradation products. A simple base cleavage of this type of linkage would produce equal quantities of both substitutents and this postulate includes, therefore, an explanation of the fact that aromatic products predominate in our degradation mixtures. It is entirely probable that aromatic moities are present in the forms of both ester and ether linkages.

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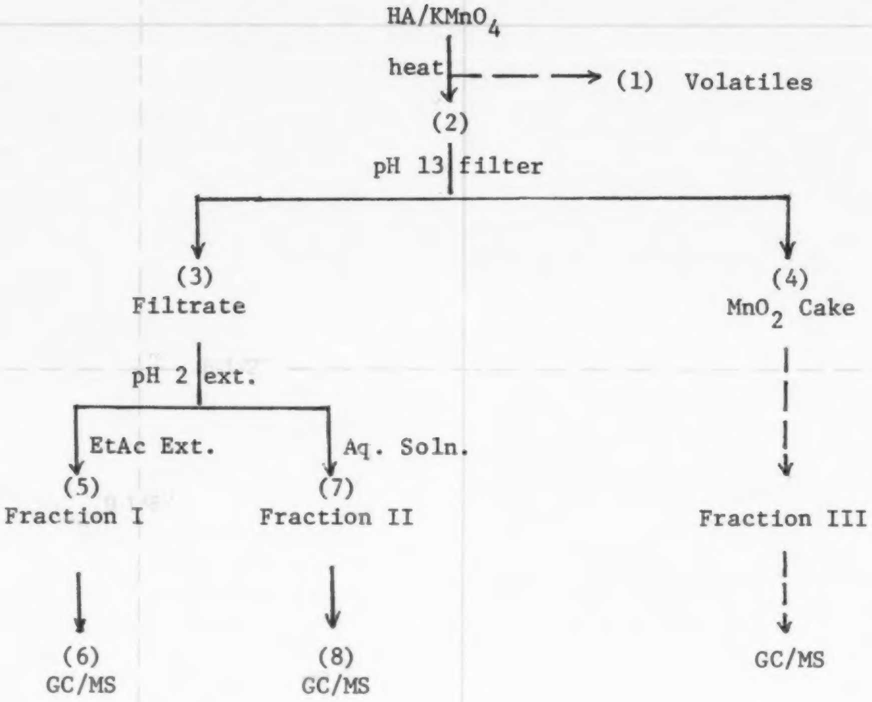
HA/KMnO$_4$
heat
(1) Volatiles
(2)
pH 13
filter
(3)
Filtrate
(4)
MnO$_2$ Cake
pH 2
ext.
EtAc Ext.
Aq. Soln.
(5)
Fraction I
(7)
Fraction II
Fraction III
(6)
GC/MS
(8)
GC/MS
GC/MS

Percent of Original TOC in Fractions.

Degradation / Fraction	HA/KMnO$_4$ 4 : 1	HA/KMnO$_4$ 2 : 1	HA/KMnO$_4$ 1 : 1.5	HA/KMnO$_4$ 1 : 4
(1)	0	0	7	12
(2)	100	100	93	88
(3)	86	88	90	83
(4)	14	12	3	5
(5)	-	-	40	28
(6)	3	11	18	15
(7)	-	-	50	55
(8)	2	4	10	9

Figure 27. Percentage distribution of degraded humic products.

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The permanganate oxidation data indicate that the principal number of alkyl constituents on the aromatic rings in the humic macromolecule is between 3 and 4 to account for the predominance of the tricarboxylic acid derivatives. If these acid substituents are present in the undegraded molecule the relative increase of tricarboxylic aromatic acids in the permanganate oxidation mixtures is not explained. Some of the acid groups must be bound in ester linkages probably with other aromatic moieties, but most of the alkyl substituents must be carbon chain lengths which resist sodium hydroxide hydrolysis. Some of the carboxylic acids must be present as free groups in the undegraded marcomolecule to account for the acidity of aquatic humic acid.

There would be two sources of dibasic acids in a theoretical structure of aquatic humics. One would be from the hydrolysis of ester linkages and the other from permanganate oxidation of carbon intermonomeric bridges. These may be of roughly equal importance in the molecule because the yield of dibasic acids increases by a factor of two when sodium hydroxide hydrolysis is followed by permanganate oxidation. In addition some of the miscellaneous compounds such as the furans must be bound in hydrolyzable ether or ester linkages.

The permanganate oxidation technique which oxidizes the alkyl side-chains and preserves the aromatic moieties results in the release of benzenecarboxylic acids and saturated aliphatic acids. The humic macromolecule was observed to be broken down into small, water-soluble pieces and the identified product yield increases progressively with increasing permanganate used. The effect of oxidant/C ratio on permanganate oxidation is shown in Figure 27, for one experiment. In this figure, for the HA/$KMnO_4$ ratio of 1:1.5, fractions 6 and 8 present those percentages of original TOC detected via the GC/MS analytical procedure (29% of original TOC). If Fraction 1 is assumed to be CO_2 then the overall accountability of degradation products is 35% of original TOC prior to degradation.

At the present time our total experience with the $KMnO_4$ degradation variables suggests that the maximum yield of GC/MS detectable degradation products (Fractions 6 and 8) is typically in the range of 20-30% of original TOC.

These findings suggest that:

- a more comprehensive and effective analytical scheme should be developed to permit detection of a wider range of degraded products that may be present. Important variables here include improved solvent extraction and methylation efficiencies as well as the use of multiple GC columns of different polarities. In addition, use of capillary GC may result in increases in the number of degradation products identified.

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- aromatic structures may account for 15-25% (wt.% as C) of the original humic structures if our present data is approximately close to optimal. This estimate results from the product of the 20-30% overall yield figure and the percentage of the total identified products that are aromatic (74-80%, see Tables 16-18 for $KMnO_4$ oxidation).

The latter is supported by the ^{13}C NMR study that aromatic carbons contribute about 17% and 30% of the carbon skeletons of FA and HA, respectively. This finding is also complemented by the ^1H NMR data that about 18% of protons are attached to aromatic rings.

It may be speculated that carbohydrates contribute to humic structures based on the following observations:

- the resonances between 70-80 ppm in ^{13}C NMR spectra are characterisitic of the oxygen-substituted carbons. H NMR also show broad resonances in the 3.4-.4 ppm region which indicate the presence of CH_3-O-, $-CH_2-O-$, $-\overset{|}{C}H-O-$ or R-OH groups.

- periodic acid has been used for the selective cleavage of carbon-carbon bonds of diols and carbohydrates since 1928. ^1H NMR (Figure 26) shows that the resonances in the 3.4-4.4 ppm region which are characteristic of protons on carbon substituted by an oxygen atom(s) almost disappear after the HA has reacted with periodic acid.

- total organic carbon measurement shows that measurable quantities (Figure 27) of the humic molecules were converted to carbon dioxide or other small volatile products in excess permanganate oxidation.

It is possible to construct a model of the intermonomeric linkages present in the undegraded Humic Acid macromolecule based on these findings. This model (Figure 28) is necessarily crude and is intended for discussion purposes only. Its principal features include:

- a base hydrolyzable fraction attached through aromatic ether and ester linkages to a base resistant core. The product of this hydrolysis must yield the aromatic moieties, mono- and dibasic acids shown in Table 16-18. The products should be predominantly aromatic to account for the relative yields shown in Table 16.

- only one out of every three base hydrolyzable aromatic fragments should be esterified with MBA or DBA to account for the relative yields shown in Tables 16-18.

- the base resistant core must represent approximately four times the relative structural importance of the hydrolyzable fragments to account for the increased yield with $KMnO_4$ (Table 16, HA/NaOH vs HA/NaOH/$KMnO_4$).

- the carbohydrates are bound with other fragments via ether, ester, H-bonding, or carbon-carbon bonds.

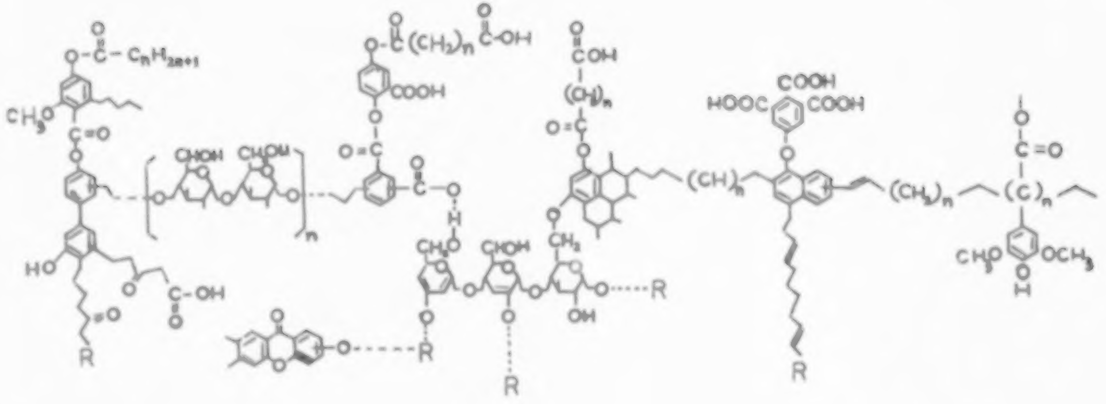
O-C-CnH2n+1
CH3O
C=O
HO
C-OH
R
CHOH
CHOH
n
O-C(CH2)nC-OH
COOH
O=C
C-O
H
CH2O
CHOH
CH2
OH
R
COOH
(CH2)n
HOOC
COOH
COOH
(CH)n
(CH2)n
(C)n
C=O
CH3O
OCH3
OH

Figure 28. Proposed model of intermonomeric linkages in a portion of undegraded humic acid macromolecule.

SECTION 7

MODEL COMPOUND SELECTION AND REACTION WITH CHLORINE

SELECTION

Compounds chosen represent three aromatic substitution patterns (Figure 29) known to exist in humic degradation products at the initiation of this study. In addition each substitution pattern was modeled with respect to alkyl substituent (propyl) and unsaturation where possible. The propyl side chain was selected because of the dominance of this unit in natural lignitic woody tissue which also contains the 3-methoxy-4-hydroxy and 3,5-dimethoxy-4-hydroxy aromatic substitution patterns.

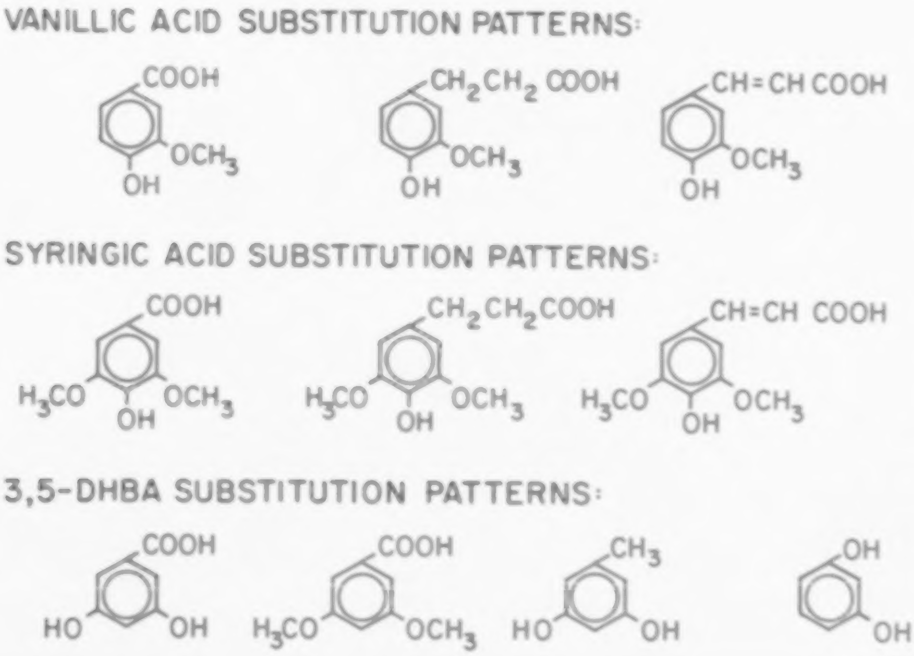
VANILLIC ACID SUBSTITUTION PATTERNS:
COOH
OCH3
OH
CH2CH2 COOH
OCH3
OH
CH=CH COOH
OCH3
OH
SYRINGIC ACID SUBSTITUTION PATTERNS:
COOH
H3CO
OH
OCH3
CH2CH2COOH
H3CO
OH
OCH3
CH=CH COOH
H3CO
OH
OCH3
3,5-DHBA SUBSTITUTION PATTERNS:
COOH
HO
OH
COOH
H3CO
OCH3
CH3
HO
OH
OH
OH

Figure 29. Model compounds chosen.

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PROCEDURES

Kinetic Studies

Each model compound was permitted to react with HOCl in a pH 7.0 buffer (K_2HPO_4/KH_2PO_4) over total time periods ranging from 20 to 250 min. The initial concentration of each model compound and the chlorine to carbon ratio (HOCl/C) employed is shown in Table 19. Individual reactions were initiated by mixing standardized concentrations prepared from known dilutions of stock 5% NaOCl (at pH 7.0) and model compound/buffer solutions in chlorine demand free water. Reaction vessels were held at ambient temperature (25°C) except for resorcinol which was held at 5°C in a constant temperature water bath. Reactions were terminated at desired time increments by the addition of standardized 0.2 $\overline{N}$ sodium arsenite and the solutions were stored in a head-space free condition prior to chloroform and chlorine demand analyses.

Chloroform analysis was carried out using the method of Bellar and Lichtenberg (152) and employed a Tracor MT-220 gas chromatograph equipped with a Hall electrolytic conductivity detector. Chlorine demand was measured using a back titration of the excess sodium arsenite with standard iodine solution.

Resorcinol Stoichiometric Study

A separate study was done to determine the stoichiometry of chloroform formation from resorcinol. The procedures used were the same as in the kinetics studies except that chlorine to carbon ratio was the variable instead of time. Resorcinol concentrations in the 300 ml. reaction solution ranged from 9.19 mg/mL at 0.0962 HOCl/C to 0.505 mg/mL at 1.96 HOCl/C mole ratios. Reactions were run at ambient temperature, and pH 7 conditions were confirmed after 24 hrs. for each reaction mixture. No chlorine quenching was performed in this experiment.

Product Identification Studies

Reaction procedures for the product identification studies were similar to those employed in the kinetic studies except that an approximate ten-fold increase in initial concentration of model compound was used. At the end of each reaction time, free available chlorine was removed by addition of crystals of sodium arsenite instead of the 0.2 $\overline{N}$ solution to minimize dilution. No arsenite was added to solutions which showed no excess chlorine. The chlorine to carbon ratios chosen were 0.5 and 2 for both resorcinol and 3-methoxy-4-hydroxy cinnamic acid.

At the completion of each reaction the aqueous solution was lowered to pH 1 with HCl and extracted with small volumes of diethyl ether. The ether extract was dried with sodium sulfate, concentrated, and an aliquot was methylated using an ether solution of diazomethane generated from N-methyl-N-nitroso-N-nitro quanidine and sodium hydroxide. Methylated and nonmethylated samples were subjected to GC/MS analysis.

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RESULTS AND DISCUSSION

The results of kinetic experiments are summarized in Table 19 and Figure 30 from which it is clear that the meta-dihydroxy substitution pattern of resorcinol produces chloroform very rapidly. The chloroform yield is almost 93% for the carbon between the two hydroxyl groups. It may be seen that this carbon is responsible for chloroform proudction by observing the structure of the cyclic diketone (153) also formed shown in Table 20.

This yield was confirmed by the detailed stoichiometric study on resorcinol whose results are shown in Figure 31. From these experiments the following equation was derived for the reaction of resorcinol with chlorine: $C_6H_6O_2 + 6.84\ (\pm 0.54)\ Cl_2 \rightarrow 1.05\ (\pm 0.05)\ CHCl_3$. These numbers represent 95% confidence intervals.

It is interesting to note that substitution of hydrogen by the simplest alkyl group (CH_3) to form orcinol (see Figure 30) does not significantly affect chloroform production. Replacement of this methyl group by carboxyl, however, produces a slight decrease in chloroform yield. In all of these cases a carbon is available between two hydroxyl groups with keto-enol resonance stabilization of the carbanion possible.

The vanillic acid structure produces much less chloroform although the chlorine demand remains relatively high. This decrease can be explained by the loss of a doubly activated carbon between two free hydroxyls. The number five carbon is still available for chloroform production and because of the p-hydroxy configuration the molecule will probably undergo oxidative decarboxylation (154) with substitution of chlorine in place of carboxyl. Continued chlorination and final cleavage could then occur at either of these chlorination sites. The syringic acid substitution pattern produces approximately ten fold less chloroform than the vanillic structure. There is no longer an available position alpha to the OH for chlorination and Larson has shown oxidative decarboxylation with chlorine substitution does not occur with syringic acid (154). The m-dimethoxy benzoic acid structure in fact produces more chloroform than syringic acid probably due to the fact that the carbon between the two methoxy groups is available for chloroform formation although this production is markedly less than resorcinol due to the lack of keto-enol stabilization. The chlorine demand data is higher for the syringic structure which may be due to the activating influence of the hydroxyl group.

Substitution of the carboxyl group by unsaturated alkyl side chains results in a general increase in both chloroform production and chlorine demand. In the case of the 3-methoxy-4-hydroxy cinnamic acid structure, we have identified decarboxylation products with and without ring substituted chlorine. This is consistent with Larson's observations (154) on the chlorination products of vanillic acid as well as the observations of Hsu and Shimizu on the chlorination of phenylpropanoids (155). When the side chain is saturated on the vanillic structure, chloroform production is reduced as is chlorine demand. With the syringic acid structure an apparent anomaly exists in that higher chloroform production and chlorine demand data were obtained for the saturated alkyl side chain.

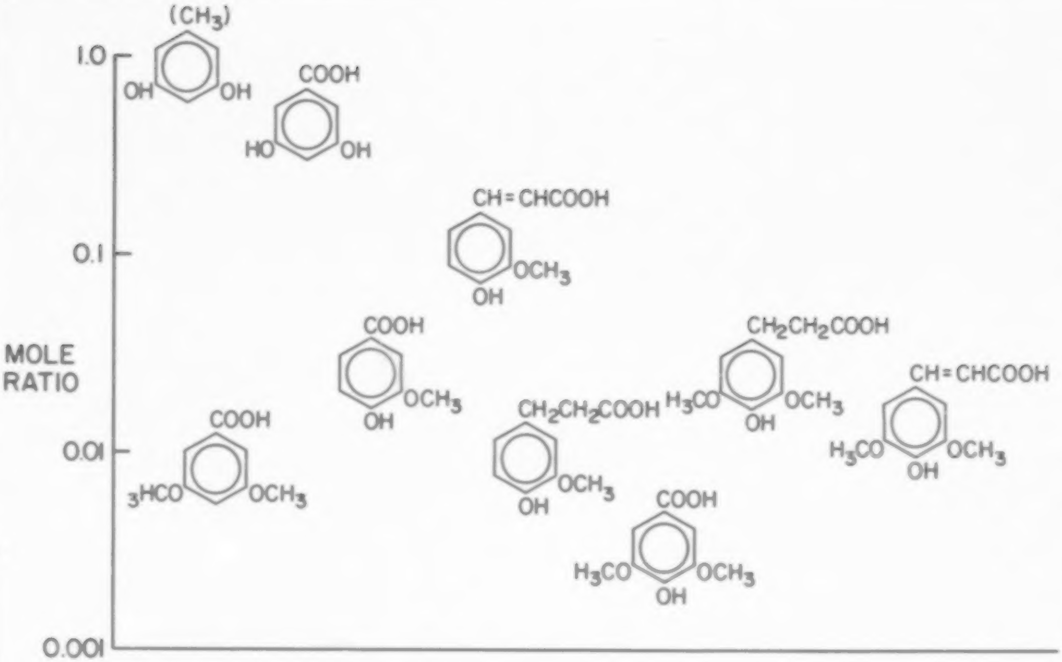

Figure 30. Relative chloroform yield from model compounds.

The actual rates of $CHCl_3$ production and chlorine consumption varied with each model compound studied, although the overall data exhibited two distinct patterns. The graphed data may be noted in Figures 33 through 42. The first pattern is typified by the orcinol data (Figure 33) and reflects a generally rapid and simultaneous exertion of both chlorine demand and $CHCl_3$ production. Compounds exhibiting this pattern include, in addition to orcinol, resorcinol, 3,5-dihydroxybenzoic acid, 3-methoxy-4-hydroxycinnamic acid, and 3,5-dimethoxybenzoic acid. These data suggest $CHCl_3$ is the primary reaction product for these model compounds. The second pattern is typified by the 3,5-dimethoxy-4-hydroxycinnamic acid data (Figure 34) and reflects an initial chlorine demand in excess of $CHCl_3$ production. Compounds exhibiting this pattern include 3-methoxy-4-hydroxy hydrocinnamic acid, syringic acid, vanillic acid, and β(3,5-dimethoxy-4-hydroxyphenyl) propionic acid. These data suggest that $CHCl_3$ is a minor reaction product for these model compounds.

The nature of reaction products other than $CHCl_3$ was investigated for two of the model compounds; resorcinol (high $CHCl_3$ and high Cl_2 demand) and 3-methoxy-4-hydroxycinnamic acid (low $CHCl_3$, high Cl_2 demand). Reaction products for these two model compounds at two different Cl_2/C ratios (Table 20) were determined with low resolution electron impact GC/MS (chlororesorcinols, DCA, and chloro-3-methoxy-4-hydroxycinnamic acid), low and high resolution electron impact GC/MS (chlorobutenedioic acid), low resolution, high resolution, and mass analyzed ion kinetic energy spectrum GC/MS (chlorocyclopentene, decarboxylated substituted cinnamic acids). In addition, trichloroacetic acid was determined using low resolution electron impact with a matching standard. We were able to identify all observed GC

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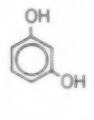
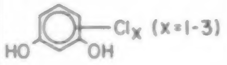
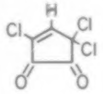
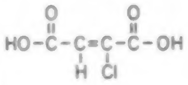
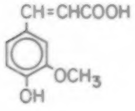
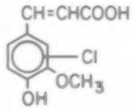
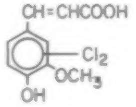
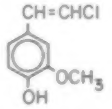
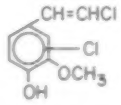
TABLE 19. RESULTS OF KINETICS STUDIES

Compound	Initial Concentration (Buffer Solution)	Cl_2/C	$CHCl_3$ Yield Moles $CHCl_3$/ Mole Compound	Chlorine Consumption Moles Cl_2/Mole Compound
1,3-dihydroxybenzene (resorcinol)	6.10 mM	1.93	0.877 (40 min.)	6.60 (40 min.)
3,5-dihydroxybenzoic acid	4.36 mM	1.95	0.450 "	7.06 "
3,5-dimethoxybenzoic acid	0.534 mM	2.00	0.00900 "	3.00 "
3,5-dihydroxytoluene (orcinol)	0.570 mM	1.82	0.852 "	6.26 "
3,5-dimethoxy-4-hydroxybenzoic acid (syringic acid)	3.35 mM	1.76	0.00502 "	5.18
3,5-dimethoxy-4-hydroxycinnamic acid	0.553 mM	1.85	0.0228 "	6.09 "
β(3,5-dimethoxy-4-hydroxyphenyl) propionic acid	0.552 mM	1.93	0.0330 "	6.06
3-methoxy-4-hydroxybenzoic acid (vanillic acid)	0.573 mM	1.73	0.0375 "	5.38 "
3-methoxy-4-hydroxy cinnamic acid	0.553 mM	1.71	0.109 "	7.63 "
3-methoxy-4-hydroxy hydrocinnamic acid	0.553 mM	1.53	0.00979 "	4.94 "

TABLE 20. REACTION PRODUCTS OF MODEL COMPOUNDS AND HOCl at 25°C

REACTANT	PRODUCTS IDENTIFIED at 0.5 Cl_2/C	PRODUCTS IDENTIFIED at 2.0 Cl_2/C
1,3-DIHYDROXYBENZENE 	  $CHCl_3$	$CHCl_3$  $HO-C(=O)-CH=CCl-C(=O)-OH$ CCl_3COOH
3-METHOXY-4-HYDROXY-CINNAMIC ACID 	    $CHCl_3$	$CHCl_3$ $CHCl_2COOH$ CCl_3COOH

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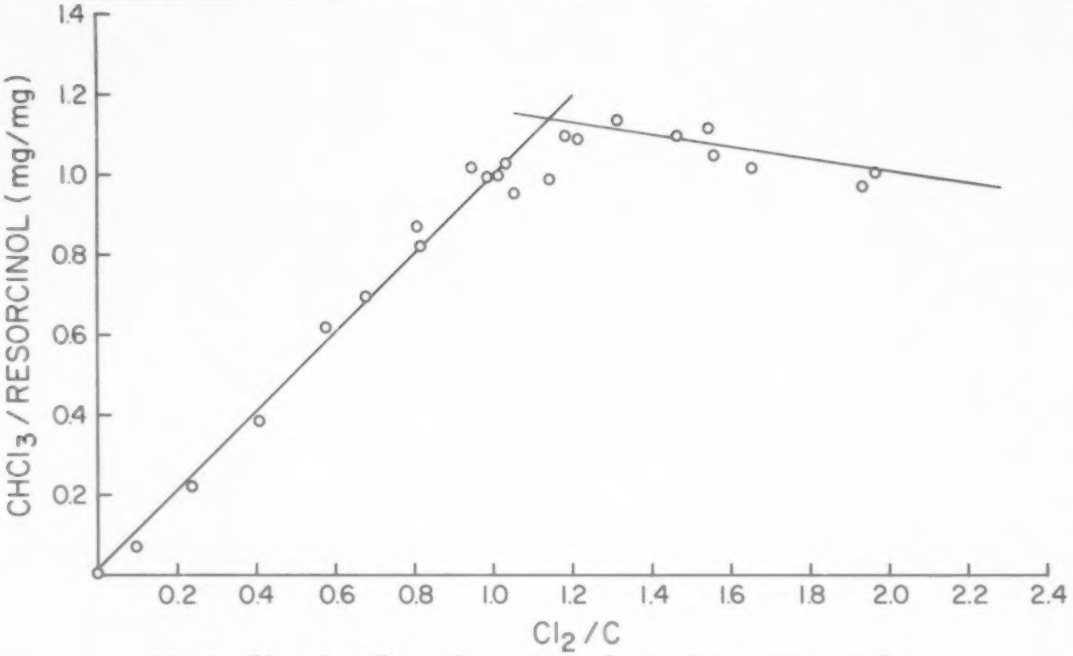

Figure 31. Results of resorcinol stochiometric study.

peaks except for one component present in the 0.5 Cl_2/C reaction of 3-methoxy -4-hydroxycinnamic acid.

Using this data a more complete picture of the reaction of chlorine with resorcinol may be obtained using the following equation:

$$C_6H_6O_2 + 7\ HOCl \rightarrow C_4H_3O_4Cl + CHCl_3 + CO_2 + 3H_2O + 3\ HCl$$

The reaction is then thought to proceed as in Figure 32.

These findings suggest that a portion of the chlorine demand is accounted for by incorporation of chlorine into non-$CHCl_3$ reaction products in addition to that demand required for $CHCl_3$ production and oxidation. Furthermore the distribution of specific forms of halogenated products is a function of the Cl_2/C dosage with high Cl_2/C ratios favoring accumulation of chlorinated acids.

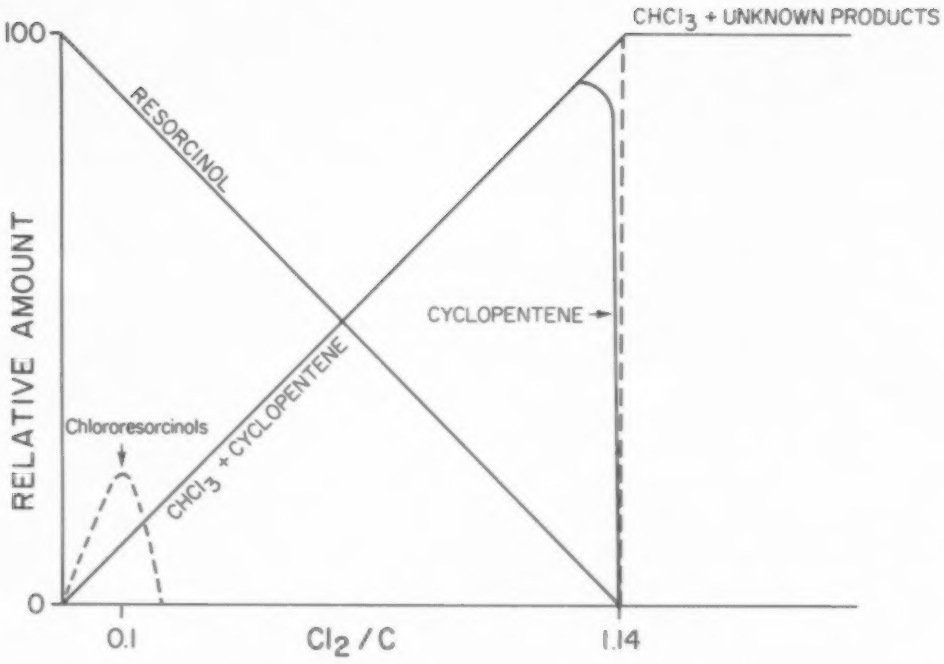

Figure 32. General interpretation of resorcinol chlorination reaction.

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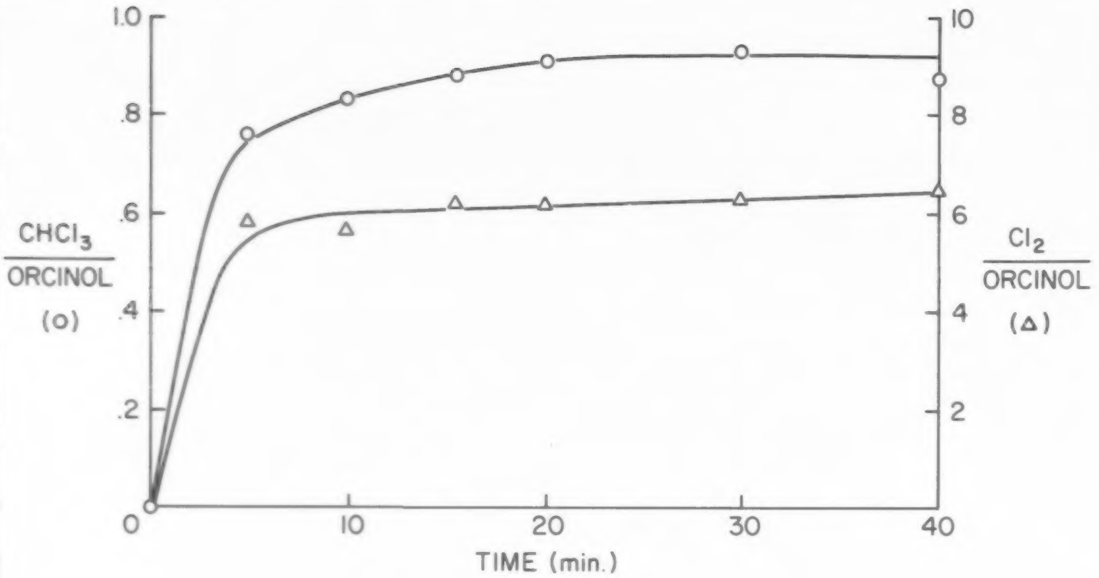

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Figure 33. Orcinol kinetic study.

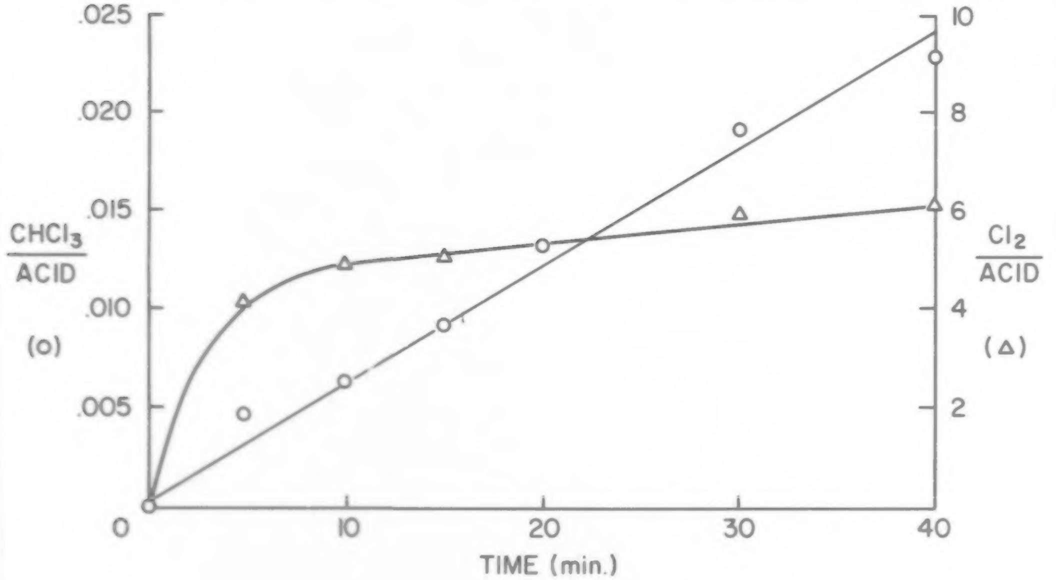

Figure 34. 3,5-dimethoxy-4-hydroxy cinnamic acid kinetic study.

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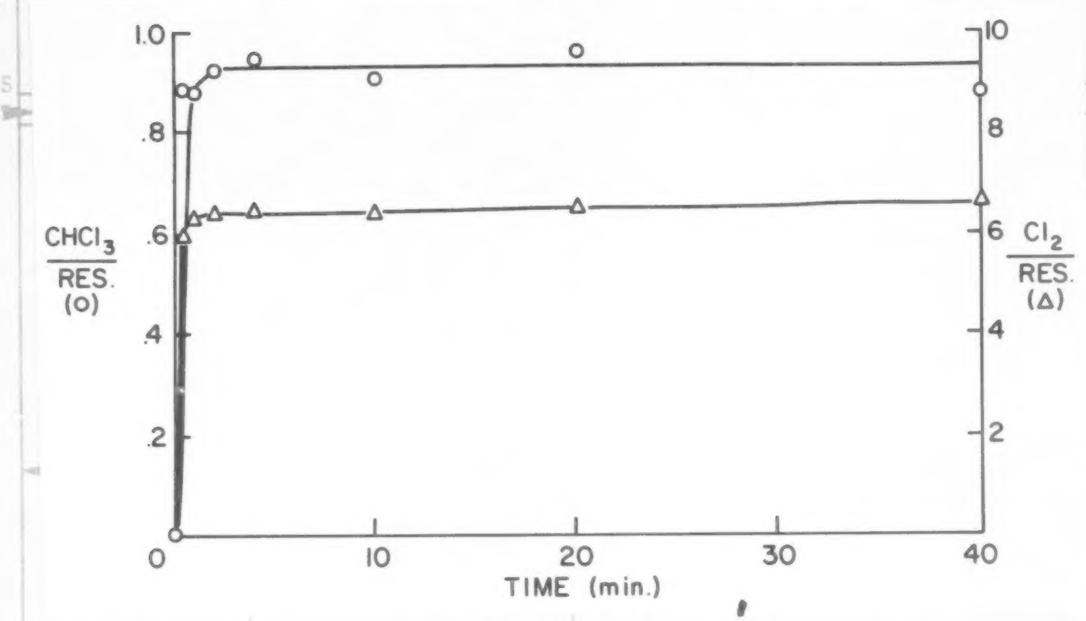

Figure 35. Resorcinol kinetic study.

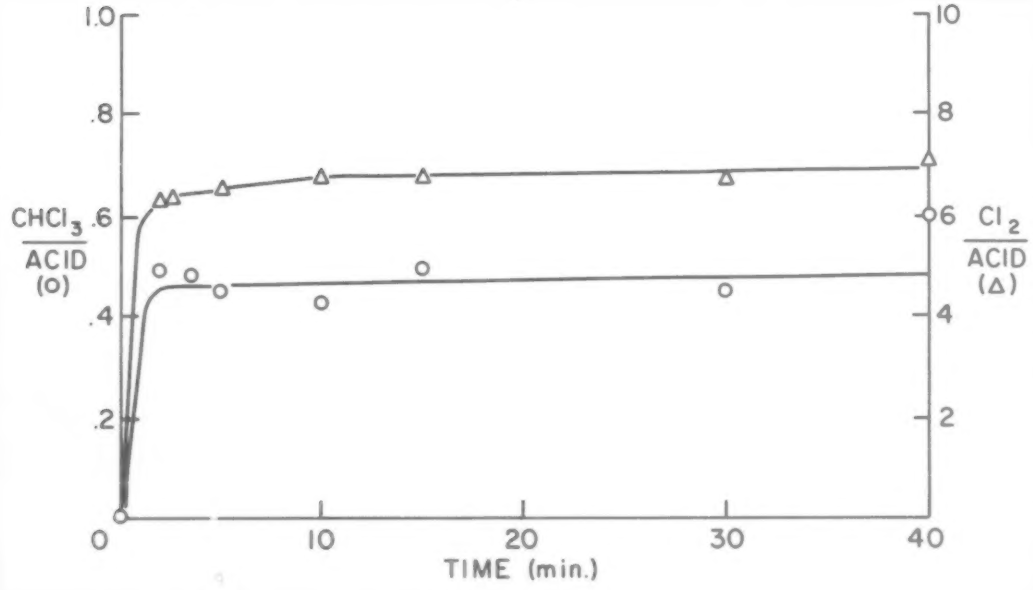

Figure 36. 3,5-dihydroxybenzoic acid kinetic study.

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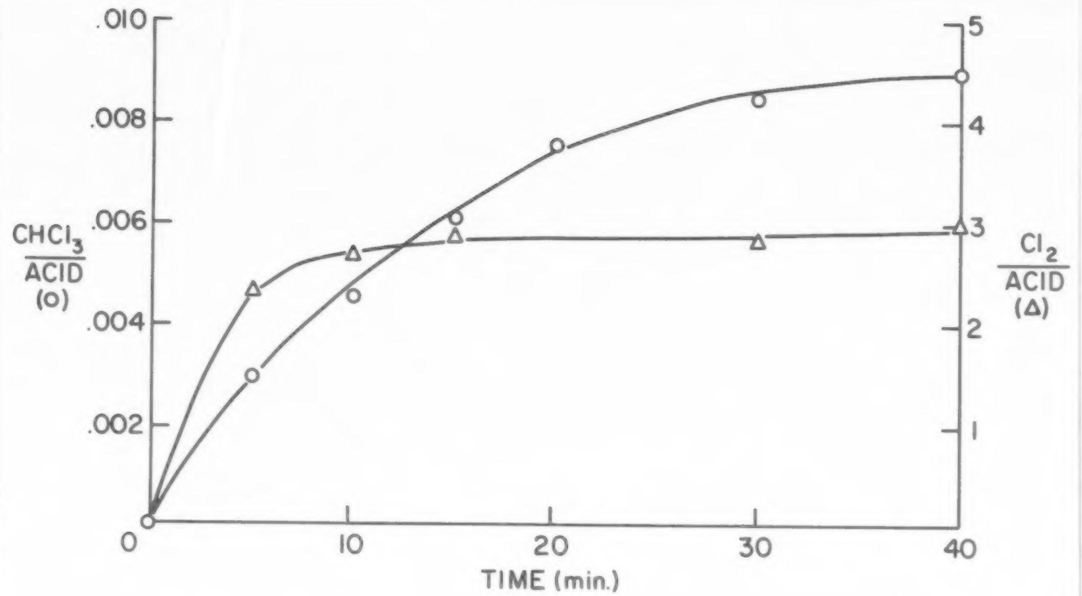

Figure 37. 3,5-dimethoxybenzoic acid kinetic study.

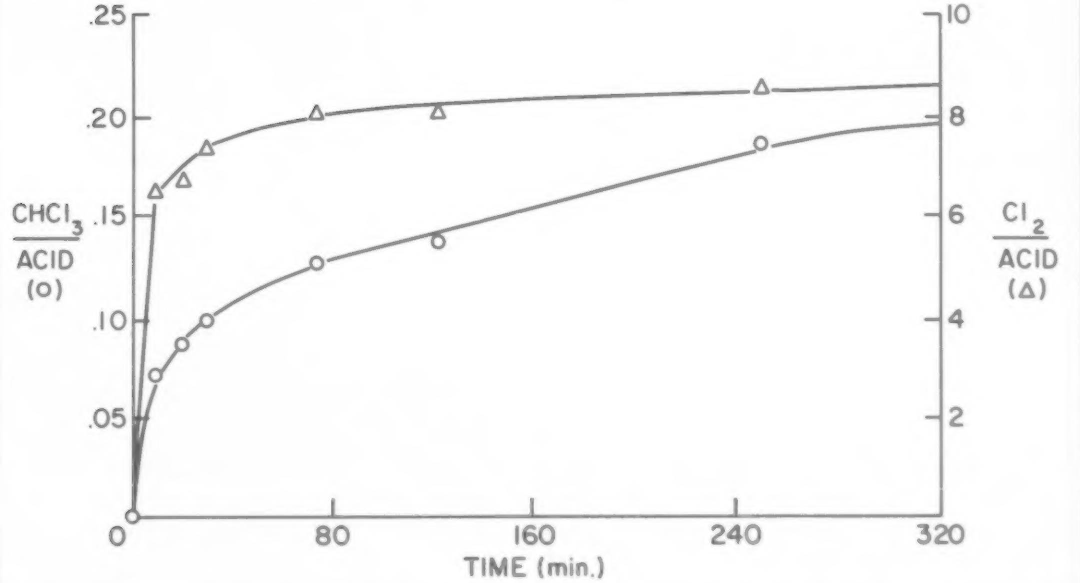

Figure 38. 3-methoxy-4-hydroxy cinnamic acid kinetic study.

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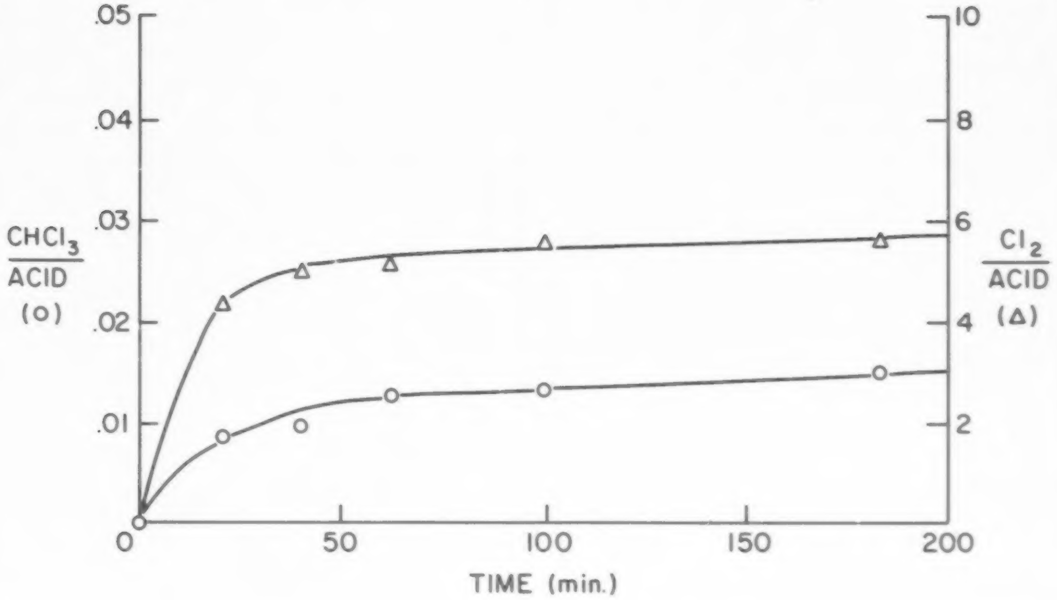

Figure 39. 3-methoxy-4-hydroxy hydrocinnamic acid kinetic study.

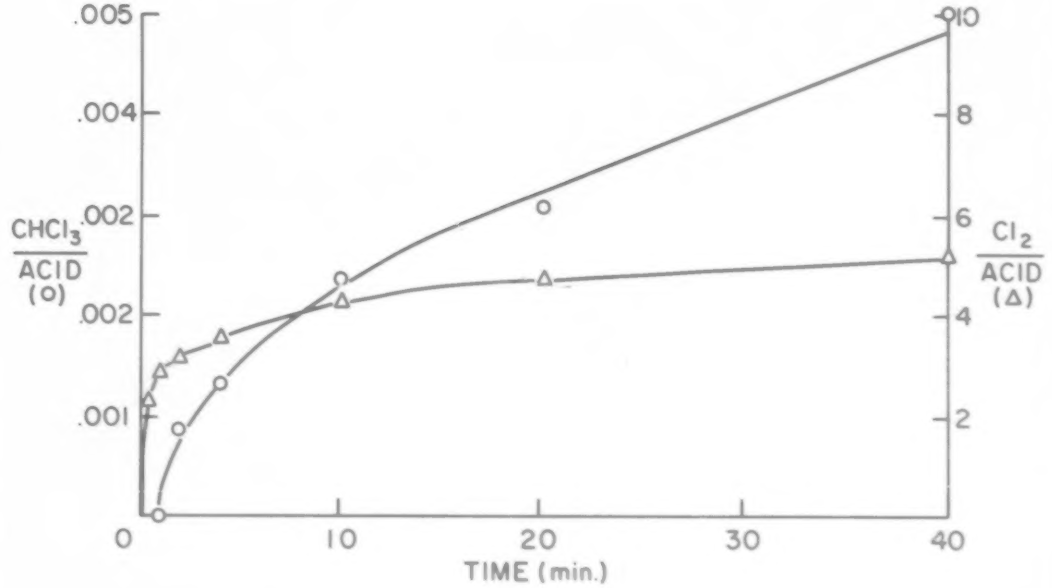

Figure 40. Syringic acid kinetic study.

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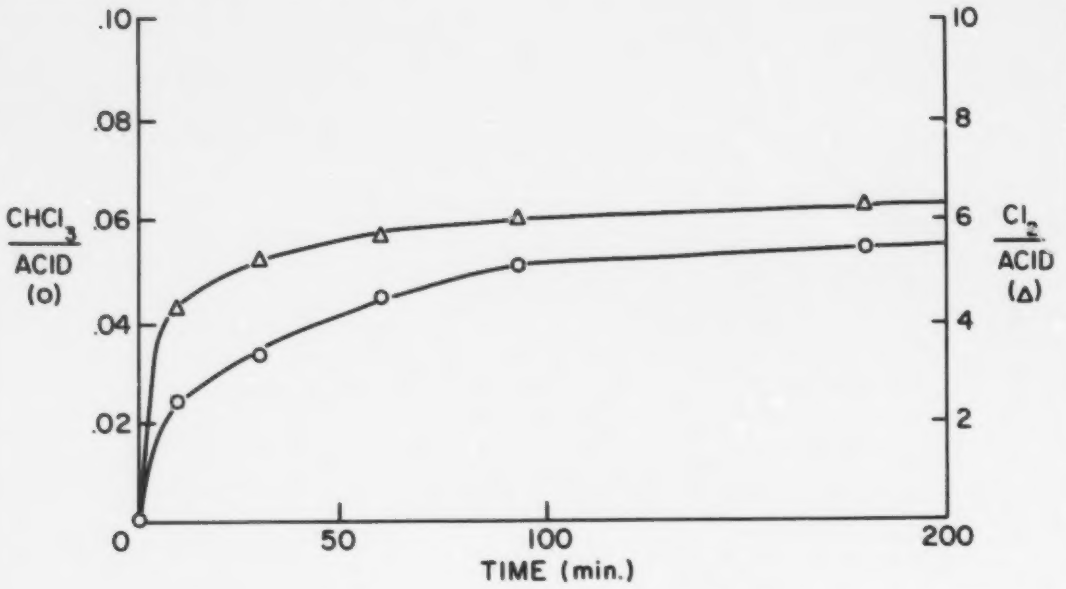

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Figure 41. Vanillic acid kinetic study.

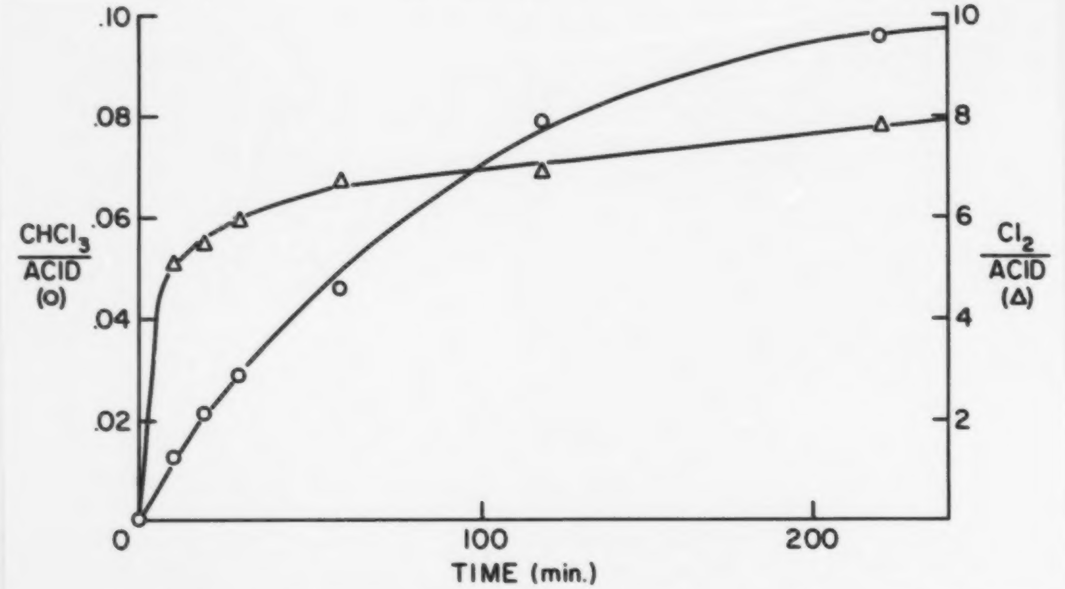

Figure 42. β(3,5-dimethoxy-4-hydroxyphenyl) propionic acid kinetic study.

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SECTION 8

CHLORINATION OF HUMIC MATERIALS

PURIFICATION OF AQUATIC HUMIC AND FULVIC ACID

Aquatic humic acid samples from Black Lake, N.C., were purified using the procedure outlined in Section 4 with the following modifications. The precipitated humic-hymatomelanic acid fractions were redissolved in 0.5 N NaOH, reprecipitated with acid and recentrifuged. After two additional precipitations the humic acid pellet was washed twice by resuspension in distilled water, acidification to pH 2.2, and centrifugation. The material obtained from this washing was freeze-dried.

Fulvic acid samples were obtained using the procedure outlined in section 6.

HUMIC ACID CONTENT OF BLACK LAKE WATER

The contribution of the humic fraction to the total organic carbon of Black Lake water was determined using a Dohrman DC 54 Total Organic Carbon Analyzer. The carbon content of a sample of Black Lake water (filtered, 10 micron) was measured before and after extraction of humic fraction. The measurements were made somewhat difficult by the presence of suspended particles in the water. Nevertheless, an average value of 18.2 ppm carbon was determined for the original water. Following precipitation of the humics this value changed to 12.8 ppm indicating that 30% of the original carbon was extracted as humic acid. An attempt to determine the fraction of TOC represented by fulvic acid was unsuccessful.

CHLORINATION OF HUMIC ACID

Procedure

After several trial experiments the following procedure was selected for chlorinating humic acid. A known weight of humic acid was dissolved in a NaOH solution which was maintained at pH 12.0. Large undissolved particles were removed from the solution by centrifugation and filtration with a 0.7 micron (effective retention) glass fiber filter. Sodium hypochlorite was then added to give chlorine to carbon ratios (moles OCl^-/moles C) varying from 1 to 3.5 (chlorine concentrations = 1580 - 7462 ppm, carbon concentrations = 278 - 1960 ppm) and the solution was stirred at ambient temperature for 48-54 hours. Concentrated HCl was then added to lower the pH to 1.0 and

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the remaining chlorine was neutralized by the addition of $NaAsO_2$. The sample was extracted sequentially with freshly distilled ether followed by freshly distilled ethyl acetate. Extracts and equal volumes of solvent blanks were dried with anhydrous sodium sulfate, cooled in ice, filtered through 0.7 micron glass fiber filters, and concentrated using a Kuderna-Danish apparatus (in the case of ether) or rotary evaporation (in the case of ethyl acetate). Methyl esters of the extracted compounds were then formed using diazomethane generated from N-methyl-N-nitroso-N-nitroguanidine according to standard procedure (156).

A lengthy period of time was spent trying to find a packed gas chromatographic system which would give the best separation of the extracted chlorination products. Porapak Q, Tenax GC, Chromosorb 101, SP-1220, SP-2100, OV-17, OV-101, OV-210 and OV-225 were all tried under various conditions on both methylated and unmethylated samples. Moderate success was obtained with the SP-1220 and OV-17 columns. It was not possible, however, to use the SP-1220 phase, although its separation of low molecular weight compounds was excellent, because of the likelihood of column bleed occurring during GC/MS analysis.

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Analysis of products from these experiments was carried out using a VG Micromass 70/70 F double focusing mass spectrometer with interfaced gas chromatograph (OV-17) and VG 2000 data system.

Results and Discussion

Figure 44 presents a reconstructed gas chromatogram for the methylated ether extract obtained in the electron impact mode. Table 22 gives the specific reaction conditions for this experiment and lists products identified along with their relative yields for both the ether and the ethyl acetate extract. Figure 45 shows a reconstructed gas chromatogram of the ethyl acetate extract from this experiment. Analysis of the mass spectral data from these two extracts indicates that they both contain similar compounds but in different relative amounts. The ethyl acetate extract seems to contain higher relative amounts of high molecular weight and high polarity compounds compared with the ether extract.

Throughout the course of these experiments considerable difficulty obtaining usable gas chromatographic separations of the ethyl acetate extract was experienced. A typical poor quality ethyl acetate extract chromatogram consists of several very poorly resolved groups of peaks. Further methylation, volume reduction and other attempts to improve the chromatography were usually fruitless. Ethyl acetate does give useful results at times, however, as can be seen from Figure 45. Why this problem exists has not yet been ascertained but it may be related to the greater extraction efficiency and higher polarity of ethyl acetate.

Chemical ionization mass spectra using methane as the reagent gas were also obtained for both extracts and proved useful in the interpretation of many of the more abundant compounds. Figure 46 shows a reconstructed gas chromatogram constructed from CI data. The sample is the same as that used to develop the chromatogram shown in Figure 45.

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Relative yields in these experiments were determined using a Sigma 1 Gas Chromatograph system with which it was possible to integrate FID response quickly and accurately. It should be noted that because of the complex nature of these chromatograms, peak areas could not be normalized and represent relative weight percentages (based on carbon).

Throughout the chlorination procedure carbon yields were monitored by measuring the total organic carbon using a Dohrman DC 54 TOC Analyzer. Extraction efficiency was determined by drying a portion of the extracts with nitrogen and measuring carbon remaining in the residue. It should be noted that some of the more volatile compounds would be expected to vaporize during this evaporation step. Yields of chromatographable compounds were calculated using the Sigma 1 gas chromatograph/data system using methyl benzoate as an external standard. Here again calculations were based on measurable carbon.

Four separate experiments were run to determine the overall yields of products observed under the stated conditions. On the average, 66% of the original carbon still remained in solution after chlorine neutralization with sodium arsenite. Only 38% of the carbon remaining from chlorine oxidation was extracted into the solvents and 32% of this extracted carbon was detectable by GC (67% of which was in the ether extract, 33% in the ethyl acetate extract). This results in an overall average yield of 8% from starting carbon.

The accuracy of the compound identifications in Table 22 was greatly enhanced by the reliability of the high resolution accurate mass determinations obtained with the MM 70/70 F system. Using this type of data, greater confidence in spectral interpretations than that obtainable by simple low resolution GC/MS is possible. As indicated in the table, final confirmation was made in some cases by comparison of spectra with pure compounds.

A later experiment essentially duplicated those reported above. The same compounds were identified in roughly the same relative amounts. A few previously undetected compounds were found, however. These compounds, most of which are early eluters on OV-17, have not yet been identified.

The data in Table 22 establish that the majority of the identified products were methyl esters. Most of these compounds were acids prior to treatment with diazomethane. This conclusion was supported by the chromatogram corresponding to the unmethylated sample in which only a few small peaks were noted. Aside from several low abundance peaks three main classes of compounds were represented in the analysis; non-chlorinated substituted aromatics, non-chlorinated straight chain acids, and chlorinated straight chain acids. The relative absence of chlorinated aromatic products and presence of non-chlorinated species shows that chlorination at pH 12 acts as an effective oxidative degradation method for humic acid structures. These types of aromatic acids have also been shown to result from the action of other oxidants such as alkaline permanganate on both aquatic and soil humics (29), noted in Section 6.

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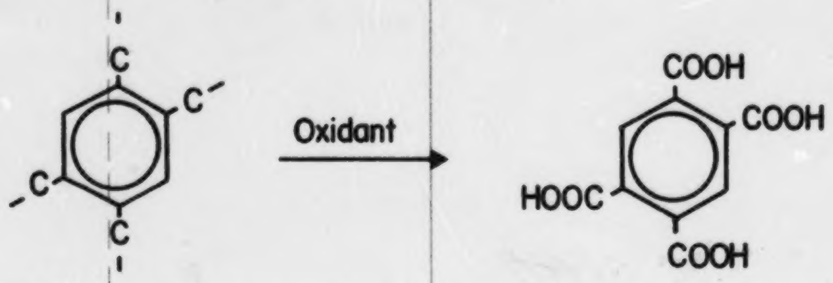
Table 22 shows a diversity of both aliphatic and aromatic di, tri, and tetracarboxylic acids. The high yields of benzene-1,2,4-tricarboxylic acid (in ether extract) and benzene-1,2,4,5-tetracarboxylic acid (in ethyl acetate extract) are consistent with a highly cross-linked structure in humic materials as postulated by Schnitzer and Khan (29):



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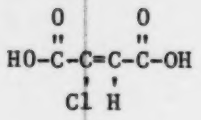
In contrast to earlier studies with alkaline hydrolysis and copper and permanganate oxidation (153,157) there is a virtual absence of phenolic and methoxy structures of the syringic and vanillic acid type. The low abundance of these structures which are activated for the electrophilic attack of chlorine suggests the high pH, excess chlorine conditions used in these experiments were sufficiently strong to open these activated aromatic rings.

Two of the most abundant compounds found in the ether extract were dichloro- and trichloroacetic acid. Other studies have shown these structures to be major products from the action of chlorine on 3-methoxy-4-hydroxycinnamic acid and resorcinol (158). Also discovered was the dicarboxylic acid:



$$HO-\overset{O}{\overset{\|}{C}}-\underset{Cl}{C}=\underset{H}{C}-\overset{O}{\overset{\|}{C}}-OH$$

which has been shown to be major chlorination product of resorcinol (158). The fact that a number of similar chlorinated and non-chlorinated small acids were present in the ether extract also supports the postulation that they are the result of ring rupture of activated aromatic structures such as vanillic and syringic acid.

The most abundant product in the ether extract was α-chloropropionic acid, which could result from aromatic ring rupture or side chain oxidation. Other chlorinated and non-chlorinated, saturated and unsaturated aliphatic mono and dicarboxylic acids were also present including higher molecular weight acids. Many of these compounds especially those in high abundance may be part of the cross linking structure of aquatic humic material.

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In a later experiment, a sample of humic acid was treated according to the modified procedure above but with no sodium hypochlorite added. The extracts obtained from the non-chlorinated pH 12 sample were found to contain chromatographable compounds, especially in the high molecular weight range. None of these compounds could be matched chromatographically with any of the chlorination products that had been previously identified.

CHLORINATION OF FULVIC ACID

Procedure

Fulvic acid was also subjected to chlorination. The humic acid chlorination procedure was used with a few minor changes which are listed below.

The fulvic acid sample was dialyzed against distilled water for 24 hours prior to chlorination using Spectra/Por 6 membranes with a molecular weight cut-off of 1000 in order to remove NaCl. The chlorine to carbon ratio (moles OCl$^-$/moles C) was set at 2.0 (chlorine concentration = 4000-4070 ppm, carbon concentrations = 336-356 ppm) and the chlorination time was 24 hours.

Results and Discussion

Figure 47 shows a reconstructed gas chromatogram (EI) of the methylated ether extract of one of these experiments. As can be seen, this chromatogram is very similar to the corresponding humic acid chromatogram (Figure 44). The interpretation of the mass spectral data (high resolution EI and CI) from this experiment is incomplete and many significant peaks have not yet been identified. Table 23 lists the compounds that have been identified to date. These are mainly compounds that could be easily matched with the corresponding humic acid sample. Additional data are needed before these compounds can be assigned definite structural formulas.

Carbon yields in the fulvic acid experiments were also monitored throughout the course of the experiments using the procedures outlined in the humic acid section of this paper. Following chlorination, an average of 72% of the original carbon still remained in solution (65-79%). Of this remaining carbon, 60% was extracted into the solvents (26% into ether, 34% into ethyl acetate) and of this extracted carbon, 39% was detectable by GC (36.5% by ether, 2.5% by ethyl acetate). This results in an overall yield of 17% from starting carbon.

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TABLE 22. NON-VOLATILE PRODUCTS OF AQUATIC HUMIC ACID CHLORINATION PRODUCT IDENTIFICATIONS AND RELATIVE YIELDS ETHER EXTRACT (METHYL ESTERS)

Reaction Conditions:
Total Volume, 320 ml
Carbon Concentrations, 420 mg/l
OCl^-/C Mole Ratio, X 1.0
Chlorination Time, 48 hr.

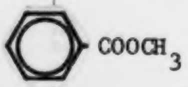
Scan. No. from Figure 44	Assigned Structure	Ether Extract[1] Relative Yield % Peak Weight (C)/ Total Weight C	Ethyl Acetate Extract[1] Relative Yield % Peak Weight (C)/ Total Weight C
7	$CH_3CH_2CH(CH_3)COOCH_3$		
	RCH_2COOCH_3	n.d.	n.d.
	R_1OCHXR_2		
11	$CH_3CHClCOOCH_3$	28.4	--
16	$CHCl_2COOCH_3$	14.7	0.5
22*	CCl_3COOCH_3	9.6	--
22	$Cl_2C=CHCOOCH_3$	n.d.	--
26,37,40	Chlorinated Aliphatic Methyl Esters	3.4	--
-	$CH_3OOCCH_2COOCH_3$	--	0.2
-	$CH_3OOCCH=CHCOOCH_3$	--	0.1
44	$CH_3OOCCH_2CH_2COOCH_3$	0.2	0.7
52*		4.1	--
63	$CH_3OOCCH=CClCOOCH_3$	1.6	5.2

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TABLE 22. Continued

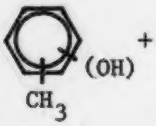
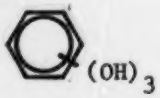
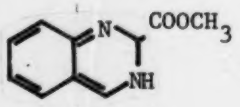
Scan No. from Figure 44	Assigned Structure	Ether Extract[1] Relative Yield % Peak Weight (C)/ Total Weight C	Ethyl Acetate Extract[1] Relative Yield % Peak Weight (C)/ Total Weight C
-	$CH_3OOCCH{=}CHCOOCH_3$	--	0.2
66	$CH_3OOCCH_2CHClCOOCH_3$	0.2	--
69	$CH_2ClCHClCOOCH_3$ or $CHCl_2CH_2COOCH_3$	0.1	--
77	Aliphatic Methyl Ester	0.3	--
84	$CH_3OOCCH{=}CClCOOCH_3$	0.4	2.2
84	$CH_3OOCC_3H_3ClCOOCH_3$ + $CH_3OOCC_2H_2Cl_2COOCH_3$	4.7	--
88	Isomer of above compounds	0.1	--
96	$CH_3OOCCCl{=}CClCOOCH_3$	0.9	--
100	$CH_3OOCC_3H_3ClCOOCH_3$ + $CH_3OOCC_3H_3RCOOCH_3$	0.5	--
115	$C_4H_9COOCH_3$	0.1	--
120,125	$C_4H_7COOCH_3$ +  + 	2.6	
151		2.3	--

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TABLE 22. Continued

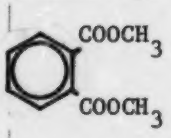
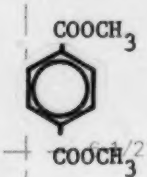
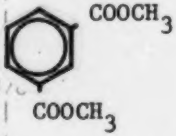
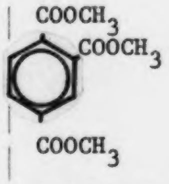
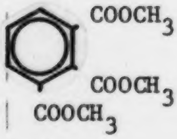
Scan No. from Figure 44	Assigned Structure	Ether Extract[1] Relative Yield % Peak Weight (C)/ Total Weight C	Ethyl Acetate Extract[1] Relative Yield % Peak Weight (C)/ Total Weight C
159*		0.9	--
163*		0.5	3.8
168		0.8	--
187	$C_6H_4(OH)(COOCH_3)$	2.9	--
198	$CH_3OOCCCl{=}C(COOCH_3)_2$	0.5	--
230	$C_{15}H_{31}COOCH_3$	1.7	--
-	$C_6(OCH_3)_6$	--	1.0
255*		5.4	14.5
-		--	2.2
258	$C_8H_9O_5Cl_3$	n.d.	--

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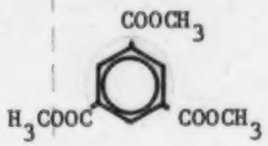
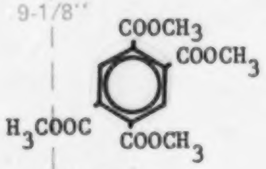
TABLE 22. Continued

Scan No. from Figure 44	Assigned Structure	Ether Extract[1] Relative Yield % Peak Weight (C)/ Total Weight C	Ethyl Acetate Extract[1] Relative Yield % Peak Weight (C)/ Total Weight C
265*		1.9	--
265	$C_6H_2(CH_3)(COOCH_3)_3$	0.2	--
274	$C_6H_2(CH_2COOCH_3)(COOCH_3)_3$ + unknown chlorine compound	0.2	--
304	$C_6H_3(COOCH_3)_3$	0.3	1.6
321*		1.0	25.2
330	$C_6H_2(COOCH_3)_4$	0.9	15.8
355	$C_6H_2(COOCH_3)_4$	0.4	--
370	$C_6H_2(COOCH_3)_4$	0.3	2.1
408	$C_6H(COOCH_3)_5$	0.3	1.3

[1] For the individual extract.

n.d.--not determined

-- not detected

*Confirmed with matching spectra

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Table 23. PRODUCT IDENTIFICATIONS AND RELATIVE YIELDS FULVIC ACID CHLORINATION

Reaction Conditions: Total Volume, 110 ml
Carbon Concentration, 337 ppm
OCl^-/C Mole Ratio, 2.0
Chlorination Time, 24 hr.

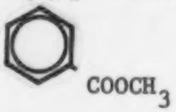
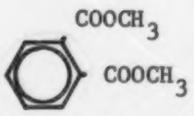
Scan. No. From Figure 47	Assigned Structure	Ether Extract Relative Yield % (Peak Weight(C)/Total Weight C)
15	$CHCl_2COOCH_3$	8.0
27	CCl_3COOCH_3	11.9
55	$CH_3OOCCH_2CH_2COOCH_3$	14.3
65		0.4
76	$CH_3OOCCH_2CHClCOOCH_3$	3.9
91	$CH_3OOCC_3H_3ClCOOCH_3$ + $CH_3OOCC_2H_2Cl_2COOCH_3$	1.6
93	$CH_3OOCC_2H_2Cl_2COOCH_3$	9.5
100	$CH_3OOCCCl{=}CClCOOCH_3$	0.9
104	$CH_3OOCC_3H_3ClCOOCH_3$ + $CH_3OOCC_3H_3RCOOCH_3$	0.4
154		0.9

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TABLE 23. Continued

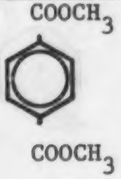
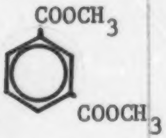
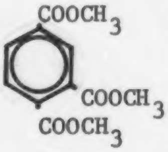
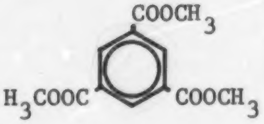
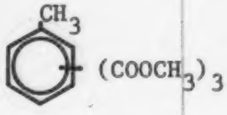
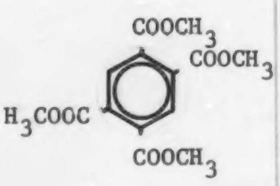
Scan. No. From Figure 47	Assigned Structure	Ether Extract Relative Yield % (Peak Weight(C)/Total Weight C)
159		0.1
162		0.9
184	$CH_3OOCCCl{=}C(COOCH_3)_2$	0.2
212	$C_{15}H_{31}COOCH_3$	1.3
230		3.2
239		1.2
241		0.1
285		1.2

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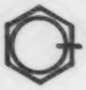
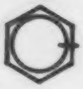
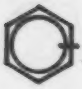
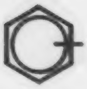
TABLE 23. Continued

Scan No. From Figure 47	Assigned Structure	Ether Extract Relative Yield % (Peak Weight(C)/Total Weight C)
294	 $(COOCH_3)_4$	1.3
302	 $(COOCH_3)_4$	0.1
322	 $(COOCH_3)_4$	n.d.
330	 $(COOCH_3)_5$	0.2

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n.d. - not determined

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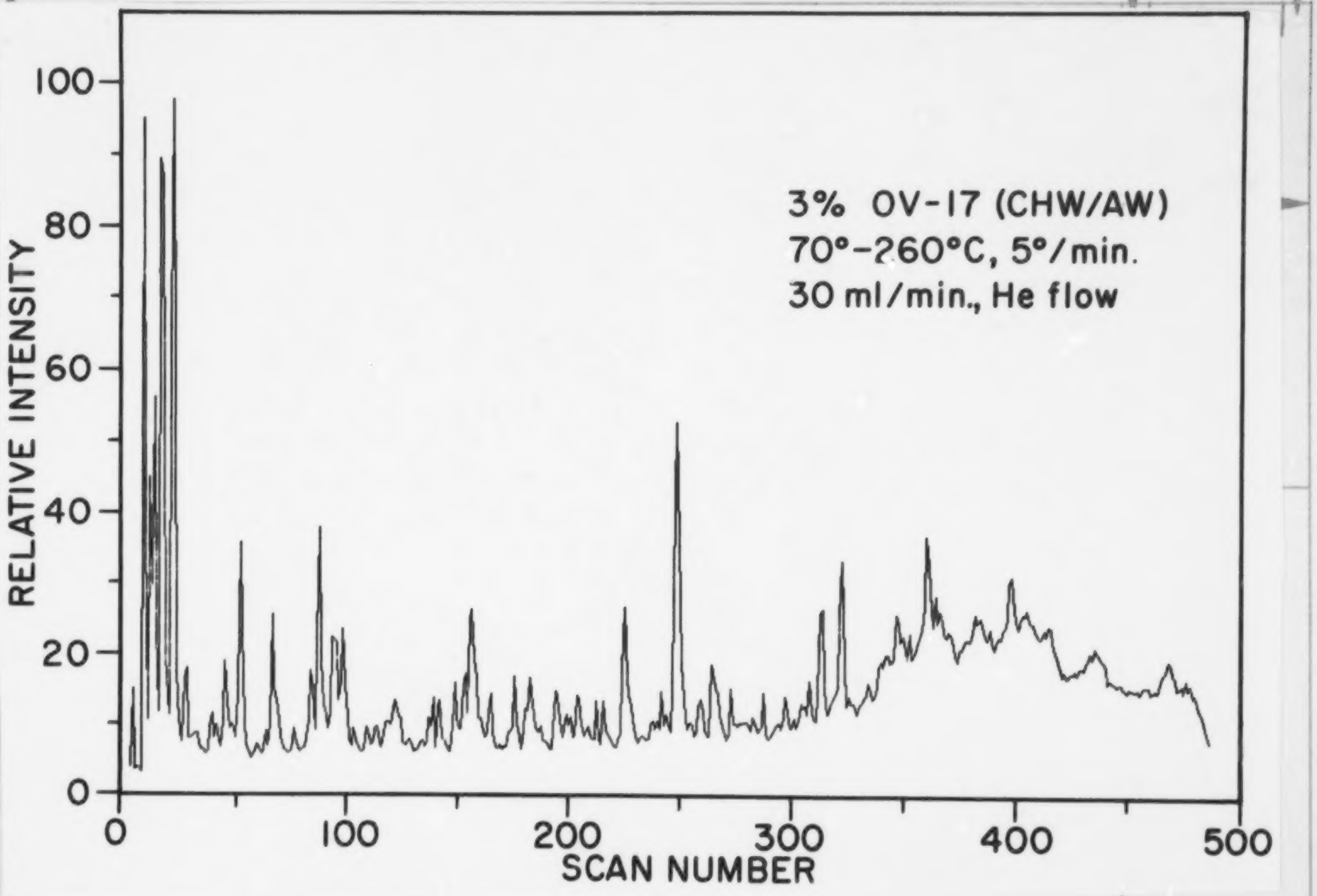

Figure 44. Reconstructed gas chromatogram of the ether extract of humic acid chlorination products.

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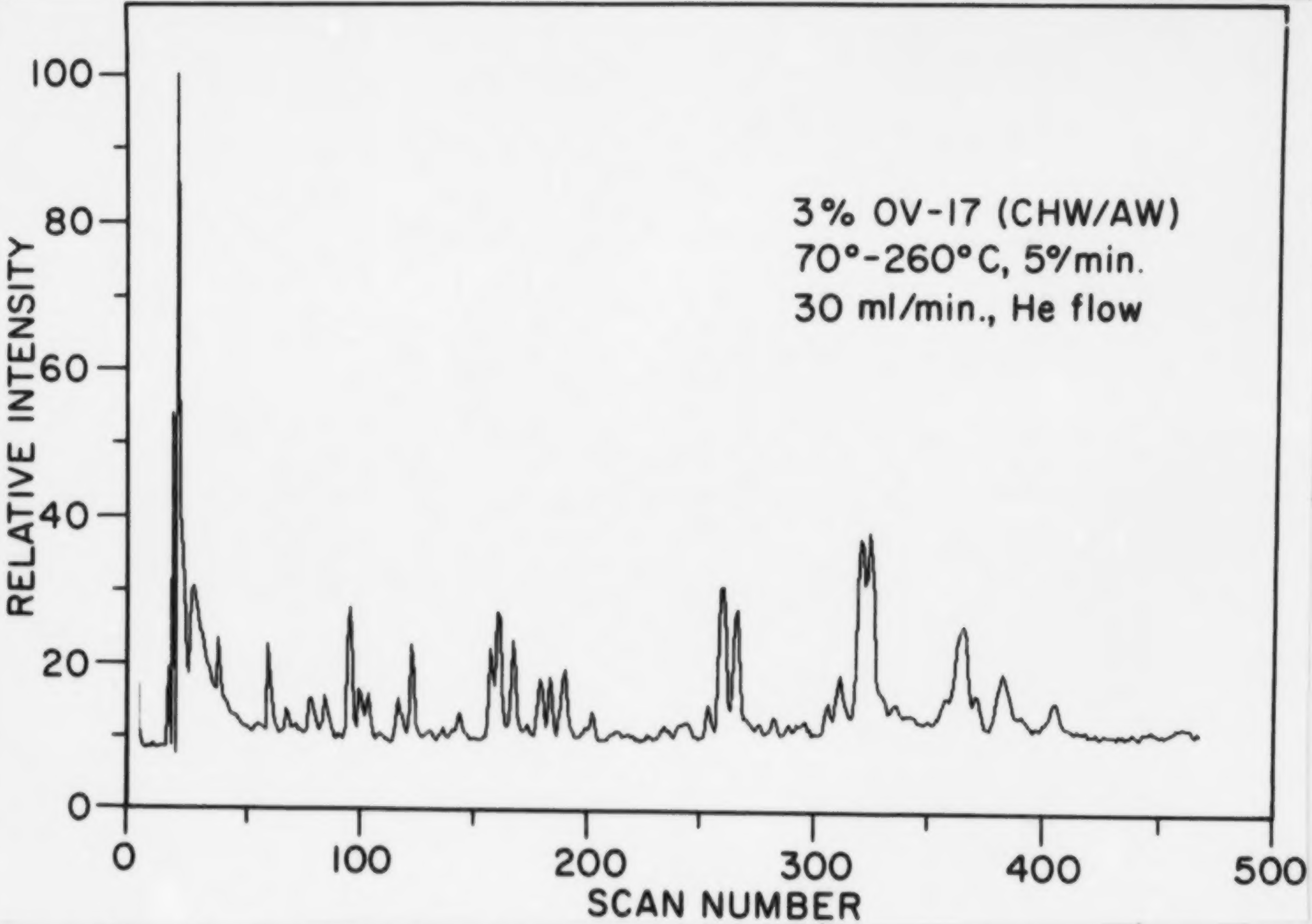

Figure 45. Reconstructed gas chromatogram of ethyl acetate extract of chlorinated humic acid.

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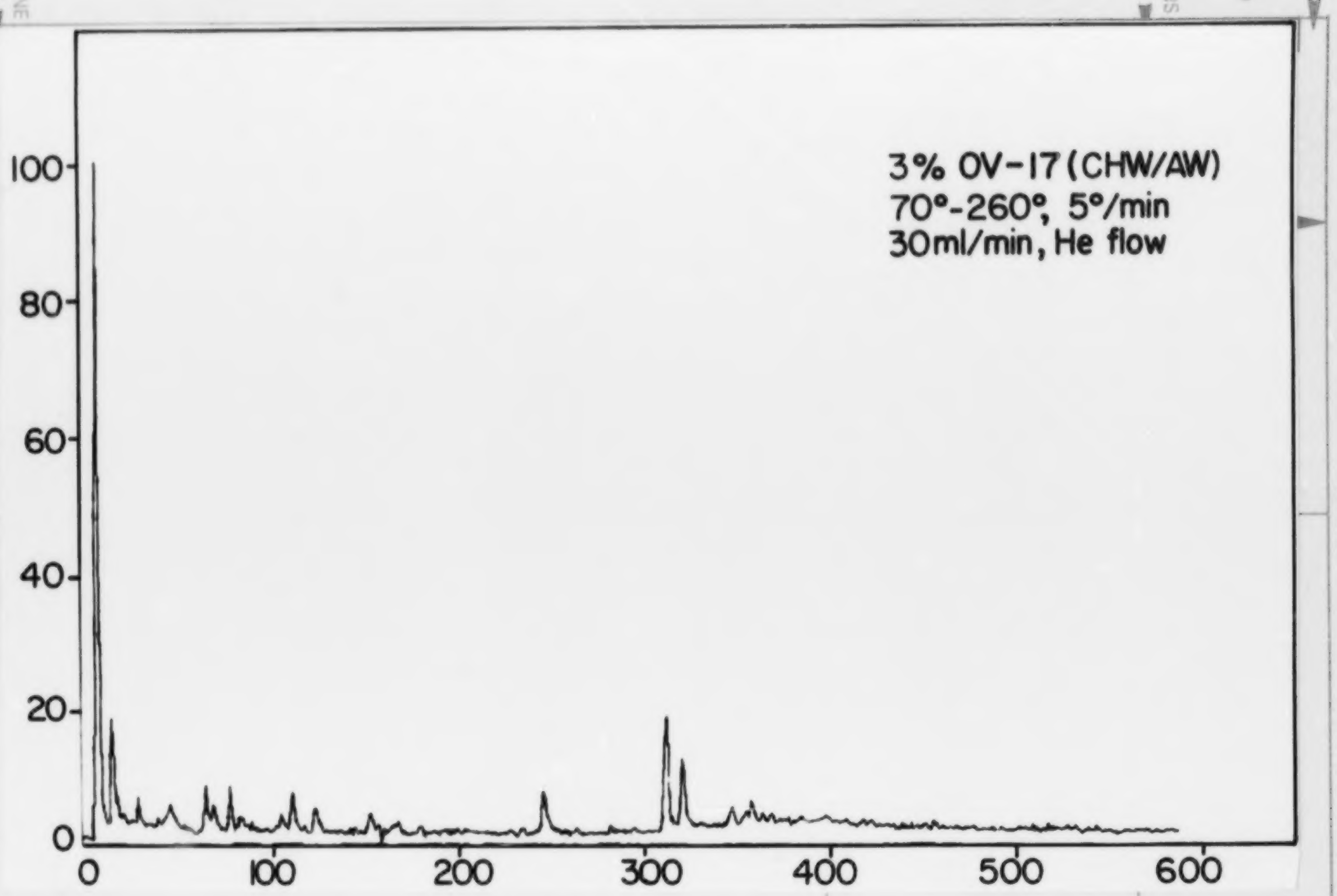

Figure 46. Reconstructed gas chromatogram of ethyl acetate extract of chlorinated humic acid using chemical ionization.

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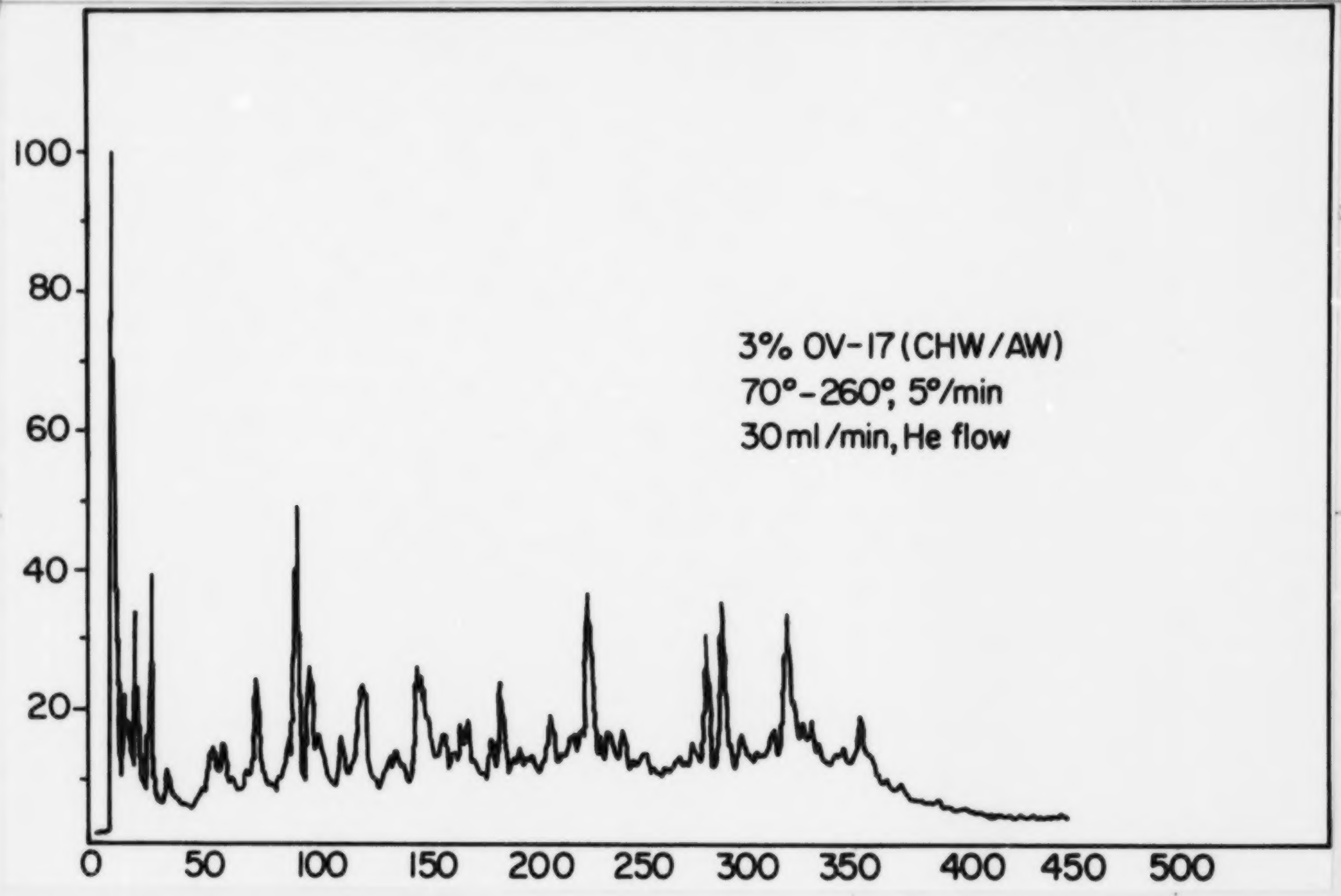

Figure 47. Reconstructed gas chromatogram of chlorinated ether extract of fulvic acid.

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APPENDIX A

SUMMARY OF INFORMATION BASES FOR STRUCTURE ASSIGNMENTS

I. STRUCTURAL INTERPRETATION OF HUMIC ACID $CuSO_4$ Degradation Products

Compound	LREI*[1]	CI*[2]	HREI*[3]	Standard (Mass Spec.)	Standard (GC Retention)	MIKE*[4]
$C_4H_9CO_2TMS$	X					
$TMSNHCH_2CO_2CH_3$	X					
Dimethoxybenzoic acid, trimethylsilylester	X					
β-methoxy-caprylic acid	X					
Phenylacetic acid	X					
Methoxybenzoic acid	X					
2-hydroxy-4-pentenoic acid	X					
P-hydroxybenzoic acid	X		X	X	X	
Vanillic acid	X		X	X	X	
3,5-dihydroxybenzoic acid	X		X	X	X	
Syringic acid	X		X	X	X	
β-hydroxy-dihydroxy-propiophenone	X					

*1 Low resolution electron impact mass spectrum
*2 Chemical ionization mass spectrum
*3 High resolution electron impact mass spectrum
*4 Mass analyzed-ion kinetic energy spectrum

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APPENDIX (continued)

II. STRUCTURAL INTERPRETATION OF HUMIC ACID NaOH HYDROLYSIS PRODUCTS

Compound	LREI	CI	HREI	Standard (Mass Spec.)	Standard (GC Retention)	MIKE
Furoic acid, methyl ester	X					
$CH_3O_2C_2H_4CO_2CH_3$	X					
$CH_3O_2C_3H_6CO_2CH_3$	X					
Benzoic acid, methyl ester	X					
Hydroxybenzoic acid, methyl ester	X					
3-phenylpropanoic acid, methyl ester	X					
$C_9H_{19}CO_2CH_3$	X					
$CH_3O_2CC_4H_8CO_2CH_3$	X					
$CH_3O_2CC_5H_{10}CO_2CH_3$	X					
Methoxybenzoic acid, methyl ester	X					
$C_{11}H_{23}CO_2CH_3$	X					
$CH_3O_2CC_6H_{12}CO_2CH_3$	X					
Benzenedicarboxylic acid, dimethyl ester	X					
$CH_3O_2CC_7H_{14}CO_2CH_3$	X					
Dimethoxybenzoic acid, methyl ester	X					
$CH_3O_2CC_8H_{16}CO_2CH_3$	X					
$C_{15}H_{31}CO_2CH_3$	X					
Benzenetricarboxylic acid, trimethyl ester (2 isomers)	X					

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APPENDIX (continued)

Compound	LREI	CI	HREI	Standard (Mass Spec.)	Standard (GC Retention)	MIKE
Methoxybenzenetricarboxylic acid, trimethyl ester (4 isomers)	X					
Benzenetetracarboxylic acid, tetramethyl ester	X					
Methoxybenzenetetracarboxylic acid, tetramethyl ester (2 isomers)	X					
Benzenepentacarboxylic acid, pentamethyl ester	X					

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III. STRUCTURAL INTERPRETATION OF FULVIC ACID NaOH HYDROLYSIS PRODUCTS

Compound	LREI	CI	HREI	Standard (Mass Spec)	Standard (GC Retention)	MIKE
$C_4H_7CO_2CH_3$	X					
$C_6H_{13}CO_2CH_3$	X					
$CH_3O_2CC_3H_6CO_2CH_3$	X					
Benzoic acid, methyl ester	X					
$CH_3O_2CC_4H_8CO_2CH_3$	X					
$C_7H_{15}CO_2CH_3$	X					
$CH_3O_2CC_5H_{10}CO_2CH_3$	X					
Methoxybenzaldehyde	X					
2-aminobenzoic acid, methyl ester	X					
Methoxybenzoic acid, methyl ester	X					
$CH_3O_2CC_6H_{12}CO_2CH_3$	X					

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APPENDIX (continued)

Compound	LREI	CI	HREI	Standard (Mass Spec.)	Standard (GC Retention)	MIKE
Hydroxybenzoic acid, methyl ester (2 isomers)	X					
$CH_3O_2C_7H_{14}CO_2CH_3$	X					
$C_{13}H_{27}CO_2CH_3$	X					
$C_{15}H_{31}CO_2CH_3$	X					
Dimethoxybenzoic acid, methyl ester (3 isomers)	X					
Methoxybenzenedicarboxylic acid, dimethyl ester (2 isomers)	X					

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IV. STRUCTURAL INTERPRETATION OF HUMIC ACID $KMnO_4$ OXIDATION PRODUCTS (EXPERIMENT 1)

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Compound	LREI	CI	HREI	Standard (Mass Spec.)	Standard (GC Retention)	MIKE
$CH_3O_2CCO_2CH_3$	X					
$CH_3O_2CCH_2CO_2CH_3$	X					
$CH_3O_2CC_2H_4CO_2CH_3$	X					
Benzoic acid, methyl ester	X					
$C_7H_{15}CO_2CH_3$	X					
$CH_3O_2CC_3H_6CO_2CH_3$	X					
$C_9H_{19}CO_2CH_3$	X					
$CH_3O_2CC_4H_8CO_2CH_3$	X					
Methoxybenzaldehyde	X					
$C_{10}H_{21}CO_2CH_3$	X					
$CH_3O_2CC_5H_{10}CO_2CH_3$	X					

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Compound	LREI	CI	HREI	Standard (Mass Spec.)	Standard (GC Retention)	MIKE
Methoxybenzoic acid, methyl ester	X					
$C_{11}H_{21}CO_2CH_3$	X					
$CH_3O_2CC_6H_{12}CO_2CH_3$	X					
$C_{12}H_{25}CO_2CH_3$	X					
Benzenedicarboxylic acid, dimethyl ester	X					
$CH_3O_2CC_7H_{14}CO_2CH_3$	X					
Dimethoxybenzaldehyde	X					
$C_{13}H_{27}CO_2CH_3$	X					
$C_{14}H_{29}CO_2CH_3$	X					
Dimethoxybenzoic acid, methyl ester	X					
$CH_3O_2CC_8H_{16}CO_2CH_3$	X					
Benzenedicarboxylic acid, dimethyl ester	X					
Methoxybenzenedicarboxylic acid, dimethyl ester (2 isomers)	X					
$C_{15}H_{31}CO_2CH_3$	X					
$CH_3O_2CC_{10}H_{20}CO_2CH_3$	X					
Benzenetricarboxylic acid, trimethyl ester (2 isomers)	X					
$CH_3O_2CC_{12}H_{24}CO_2CH_3$	X					
Methoxybenzenetricarboxylic acid, trimethyl ester (3 isomers)	X					

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Compound	LREI	CI	HREI	Standard (Mass Spec.)	Standard (GC Retention)	MIKE
Benzenetetracarboxylic acid, tetramethyl ester (3 isomers)	X					
Methoxybenzenetetracarboxylic acid, tetramethyl ester	X					
Benzenepentacarboxylic acid, pentamethyl ester	X					
Benzenehexacarboxylic acid, hexamethyl ester	X					

V. STRUCTURAL INTERPRETATION OF HUMIC ACID $KMnO_4$ OXIDATION PRODUCTS (EXPERIMENT 2)

Compound	LREI	CI	HREI	Standard (Mass Spec.)	Standard (GC Retention)	MIKE
$CH_3O_2CCO_2CH_3$	X	X	X			
$CH_3O_2CCH_2CO_2CH_3$	X	X	X			
$CH_3O_2CC_2H_4CO_2CH_3$	X	X	X			
Benzenetricarboxylic acid, trimethyl ester	X	X	X			
Methoxybenzenetricarboxylic acid, trimethyl ester (3 isomers)	X	X	X			
Benzenetetracarboxylic acid, tetramethyl ester (3 isomers)	X	X	X			
Dimethoxybenzenetricarboxylic acid, trimethyl ester	X	X	X			
Trihydroxybenzenetricarboxylic acid, trimethyl ester	X	X	X			

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APPENDIX (continued)

Compound	LREI	CI	HREI	Standard (Mass Spec.)	Standard (GC Retention)	MIKE
Methoxybenzenetetracarboxylic acid, tetramethyl ester (2 isomers)	X	X	X			
Dimethoxybenzenetetracarboxylic acid, tetramethyl ester (2 isomers)	X	X	X			
Benzenepentracarboxylic acid, pentamethyl ester	X	X	X			
Dimethoxybenzenedicarboxylic acid, dimethyl ester	X	X	X			

VI. STRUCTURAL INTERPRETATION OF HUMIC ACID $KMnO_4$ OXIDATION PRODUCTS (EXPERIMENT 3)

Compound	LREI	CI	HREI	Standard (Mass Spec.)	Standard (GC Retention)	MIKE
$CH_3O_2CCO_2CH_3$	X	X	X			
$CH_3COCHOHCH_2OCH_3$	X	X				
$C_2H_5CH(CH_3)CO_2CH_3$	X	X	X			
$CH_3O_2CCH_2CO_2CH_3$	X	X	X			
$CH_3O_2CCH(CH_3)CO_2CH_3$	X	X	X			
$CH_3O_2CC_2H_4CO_2CH_3$	X	X	X			
$CH_3O_2CC_3H_6CO_2CH_3$	X	X	X			
Methoxybenzoic acid, methyl ester	X	X	X			
Benzenedicarboxylic acid, dimethyl ester (3 isomers)	X	X	X			
Methoxybenzenetricarboxylic acid, trimethyl ester (2 isomers)		X				

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APPENDIX (continued)

Compound	LREI	CI	HREI	Standard (Mass Spec.)	Standard (GC Retention)	MIKE
Benzenetetracarboxylic acid, tetramethyl ester		X				
Methoxybenzenedicarboxylic acid, dimethyl ester		X				
Methoxybenzenetetra carboxylic acid, tetramethyl ester	X	X				
Benzenepentacarboxylic acid, pentamethyl ester	X		X			

VII. STRUCTURAL INTERPRETATION OF FULVIC ACID $KMnO_4$ OXIDATION PRODUCTS

Compound	LREI	CI	HREI	Standard (Mass Spec.)	Standard (GC Retention)	MIKE
$CH_3O_2CC_2H_4CO_2CH_3$	X					
$CH_3O_2CC_3H_6CO_2CH_3$	X					
Benzoic acid, methyl ester	X					
$CH_3O_2CC_4H_8CO_2CH_3$	X					
$CH_3O_2CC_5H_{10}CO_2CH_3$	X					
Benzenedicarboxylic acid, dimethyl ester (3 isomers)	X					
$C_{15}H_{31}CO_2CH_3$	X					
Benzenetricarboxylic acid, trimethyl ester (3 isomers)	X					
Benzenetetracarboxylic acid, tetramethyl ester	X					

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APPENDIX (continued)

VIII. STRUCTURAL INTERPRETATION OF MODEL COMPOUND CHLORINATION PRODUCTS

Compound	LREI	CI	HREI	Standard (Mass Spec.)	Standard (GC Retention)	MIKE
Monochlororesorcinol	X					
Dichlororesorcinol	X					
Trichlororesorcinol	X					
3,5,5-trichlorocyclopent-3-ene-1,2-dione	X		X			X
Trichloroacetic acid	X			X		
Dichloroacetic acid	X					
Monochloro-3-methoxy-4-hydroxycinnamic acid	X					
Dichloro-3-methoxy-4-hydroxycinnamic acid	X					
β-chloro-3-methoxy-4-hydroxymonochlorostyrene	X					X
β-chloro-3-methoxy-4-hydroxydichlorostyrene	X					X
Monochlorobutenedioic acid	X					

IX. STRUCTURAL INTERPRETATION OF HUMIC ACID CHLORINATION PRODUCTS

Compound	LREI	CI	HREI	Standard (Mass Spec.)	Standard (GC Retention)	MIKE
$CH_3CH_2CH(CH_3)CO_2CH_3$	X	X	X			
$CH_3CHClCO_2CH_3$	X	X	X			
$CHCl_2CO_2CH_3$	X	X	X			
$CCl_3CO_2CH_3$	X	X	X		X	
$Cl_2C{=}CHCO_2CH_3$	X	X	X			

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APPENDIX (continued)

Compound	LREI	CI	HREI	Standard (Mass Spec.)	Standard (GC Retention)	MIKE
$CH_3O_2CCH_2CO_2CH_3$	X	X	X			
$CH_3O_2CCH{=}CHCO_2CH_3$	X	X	X			
$CH_3O_2CC_2H_4CO_2CH_3$	X	X	X		X	
Benzoic acid, methyl ester	X	X	X		X	
$CH_3O_2CCH{=}CClCO_2CH_3$	X	X	X			
$CH_3O_2CCH_2CHClCO_2CH_3$	X	X	X			
$CH_3O_2CC_3H_3ClCO_2CH_3$	X	X	X			
$CH_3O_2CC_2H_2Cl_2CO_2CH_3$	X	X	X			
$CH_3O_2CCCl{=}CClCO_2CH_3$	X	X	X			
$C_4H_9CO_2CH_3$	X	X	X			
$C_4H_7CO_2CH_3$	X	X	X			
Trihydroxybenzene	X	X	X			
Methylphenol	X	X	X			
Phthalic acid, dimethyl ester	X		X		X	
Terephthalic acid, dimethyl ester	X		X		X	
Isophthalic acid, dimethyl ester	X		X		X	
Hydroxybenzoic acid, methyl ester	X		X			
$CH_3O_2CCCl{=}C(CO_2CH_3)_2$	X		X			
$C_{15}H_{31}CO_2CH_3$	X		X			
Hexamethoxybenzene	X		X			

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APPENDIX (continued)

Compound	LREI	CI	HREI	Standard (Mass Spec.)	Standard (GC Retention)	MIKE
Benzenetricarboxylic acid, trimethyl ester (3 isomer)	X		X		X	
Trimethylbenzenetricarboxylic acid, trimethyl ester	X		X			
1,2,4,5-Benzenetetracarboxylic acid, tetramethyl ester	X		X		X	
Benzenetetracarboxylic acid, tetramethyl ester (2 isomers)	X		X			
Benzenepentacarboxylic acid, pentamethyl ester	X		X			

X. STRUCTURAL INTERPRETATION OF FULVIC ACID CHLORINATION PRODUCTS

Compound	LREI	CI	HREI	Standard (Mass Spec.)	Standard (GC Retention)	MIKE
$CHCl_2CO_2CH_3$			X			
$CCl_3CO_2CH_3$			X			
$CH_3O_2CC_2H_4CO_2CH_3$			X			
Benzoic acid, methyl ester			X			
$CH_3O_2CCH_2CHClCO_2CH_3$			X			
$CH_3O_2CC_3H_3ClCO_2CH_3$			X			
$CH_3O_2CC_2H_2Cl_2CO_2CH_3$			X			
$CH_3O_2CC_2H_2Cl_2CO_2CH_3$			X			
$CH_3O_2CCCl_2=CClCO_2CH_3$			X			
$CH_3O_2CC_3H_3ClCO_2CH_3$			X			

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APPENDIX (continued)

Compound	LREI	CI	HREI	Standard (Mass Spec.)	Standard (GC Retention)	MIKE
$CH_3O_2CCCl{=}C(CO_2CH_3)_2$			X			
$C_{15}H_{31}CO_2CH_3$			X			
Phthalic acid, dimethyl ester			X			
Terephthalic acid, dimethyl ester			X			
Isophthalic acid, dimethyl ester			X			
1,3,4-Benzenetricarboxylic acid, trimethyl ester			X			
1,3,5-Benzenetricarboxylic acid, trimethyl ester			X			
Methylbenzenetricarboxylic acid, trimethyl ester			X			
1,2,4,5-Benzenetetracarboxylic acid, tetramethyl ester			X			
Benzenetetracarboxylic acid, tetramethyl ester (2 isomers)			X			
Benzenepentacarboxylic acid, pentamethyl ester			X			

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9-1/8"
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EPA-287 (Cin.)
(4-76)

APPENDIX B

SAMPLE BAR GRAPH MASS SPECTRA

Computer reconstructed electron impact mass spectra of ten compounds representing examples from all phases of the work are shown in the following pages.

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EPA-287 (Cin.)
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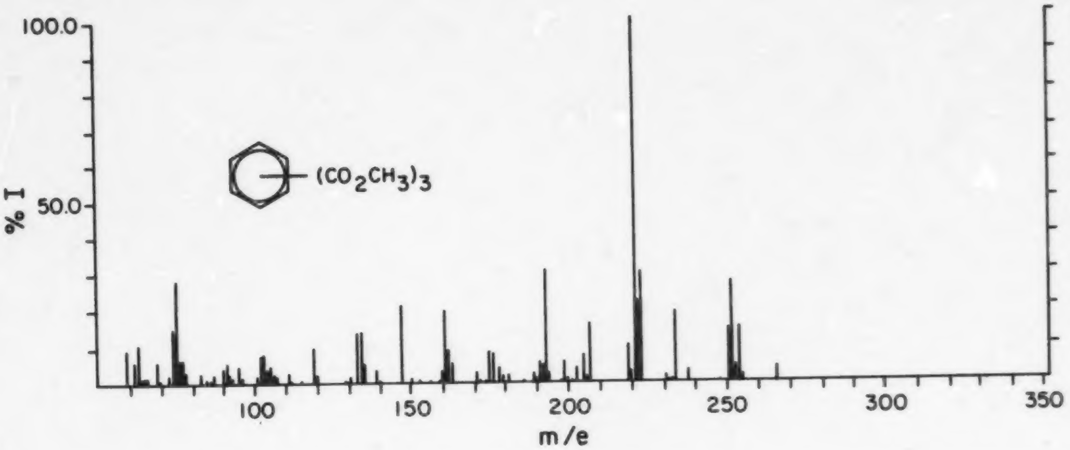

Figure B-48. Mass spectrum of an isomer of benzene tricarboxylic acid methyl ester.

9-1/8"

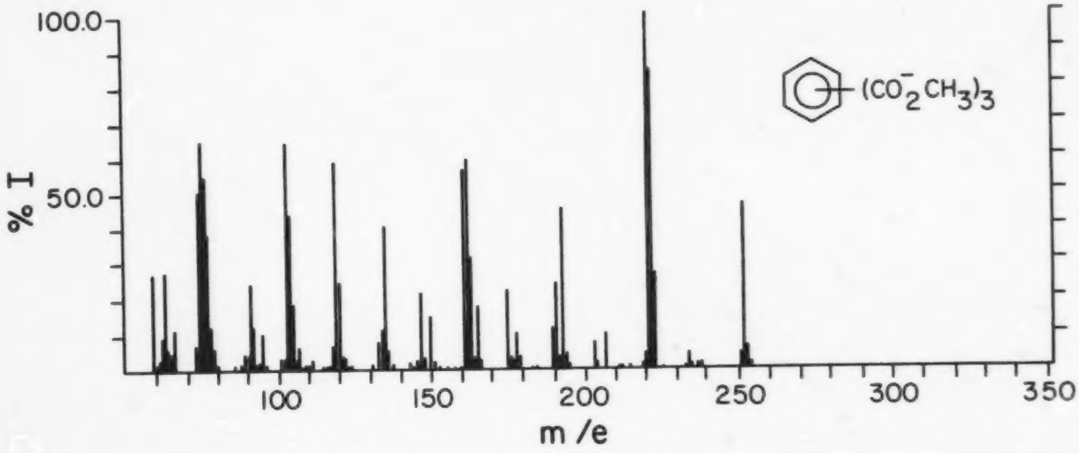

Figure B-49. Mass spectrum of a second isomer of benzene tricarboxylic acid methyl ester.

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EPA-287 (Cin.)
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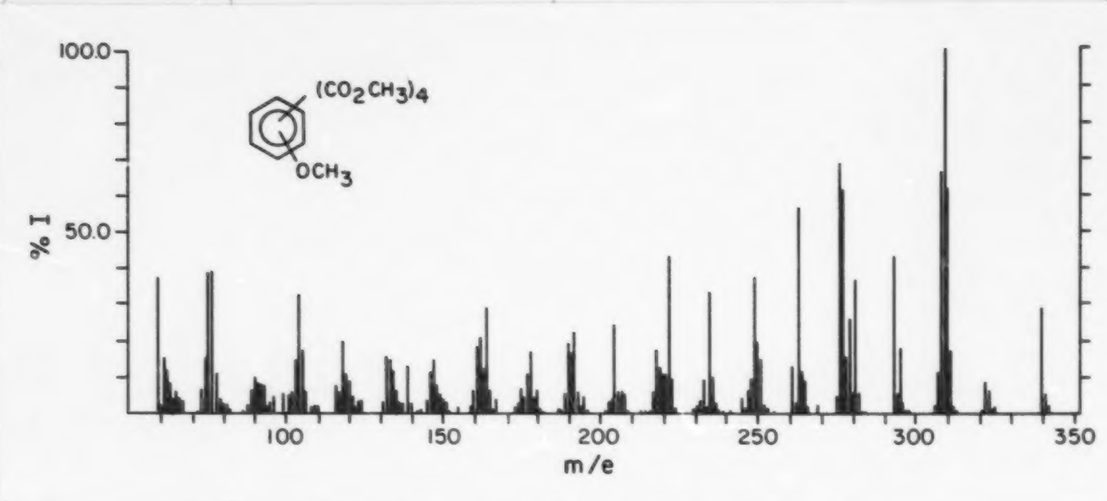

Figure B-50. Mass spectrum of a methoxy benzene tetracarboxylic acid methyl ester,

9-1/8"

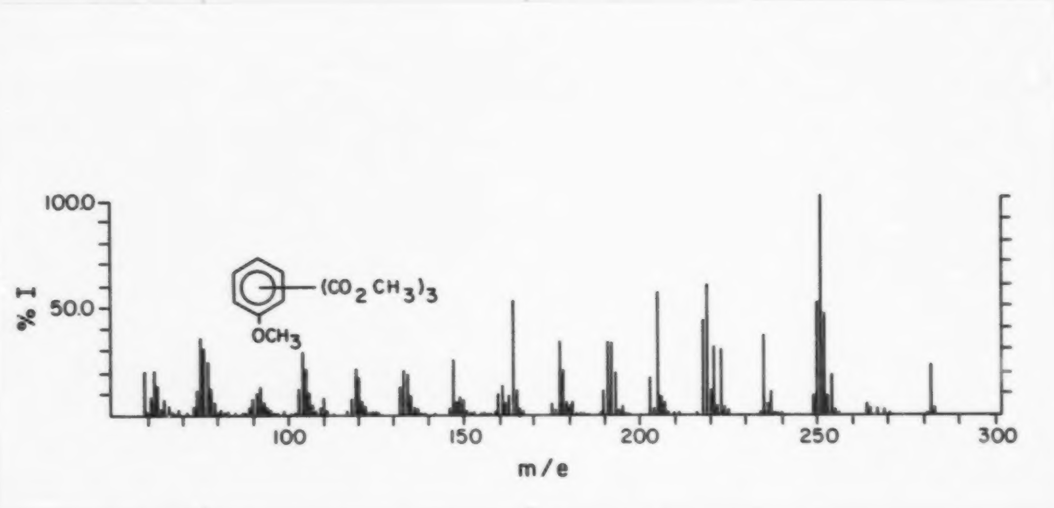

Figure B-51. Mass spectrum of a methoxy benzene tricarboxylic acid methyl ester.

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(4-76)

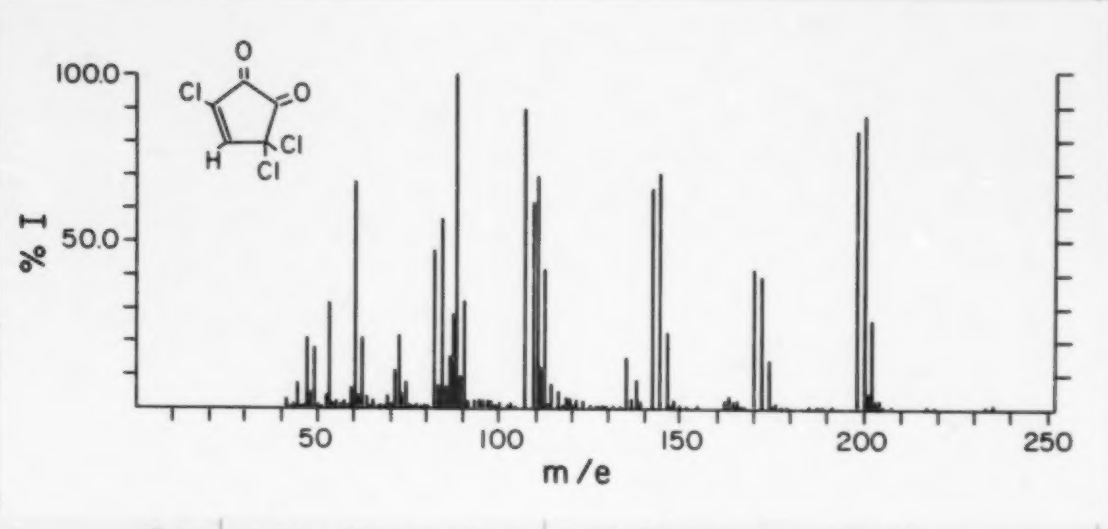

Figure B-52. Mass spectrum of trichlorocyclopentenedione.

9-1/8"

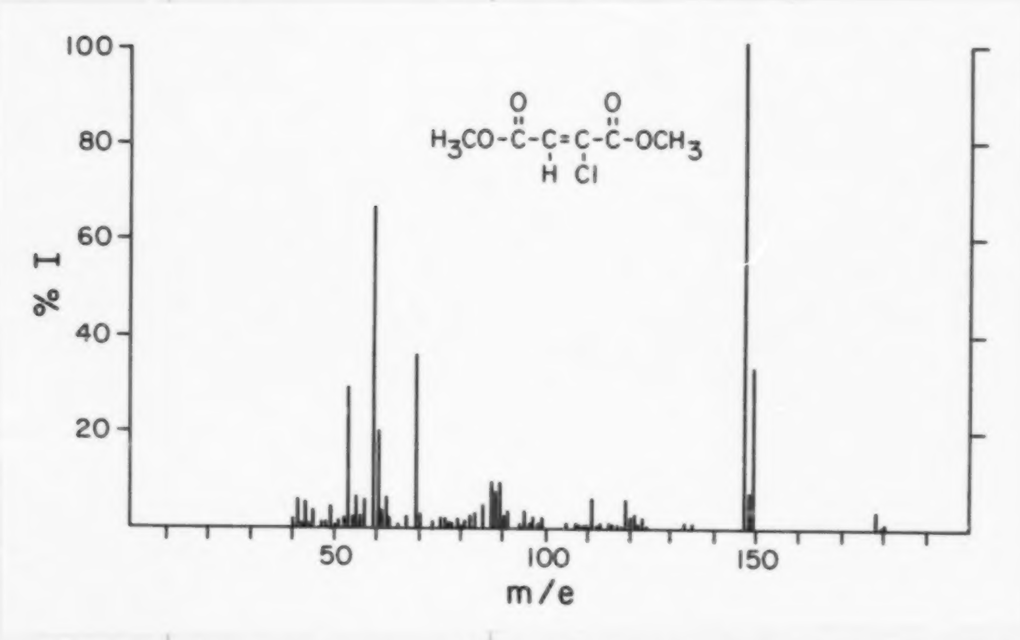

Figure B-53. Mass spectrum of chlorobutenedioic acid dimethyl ester.

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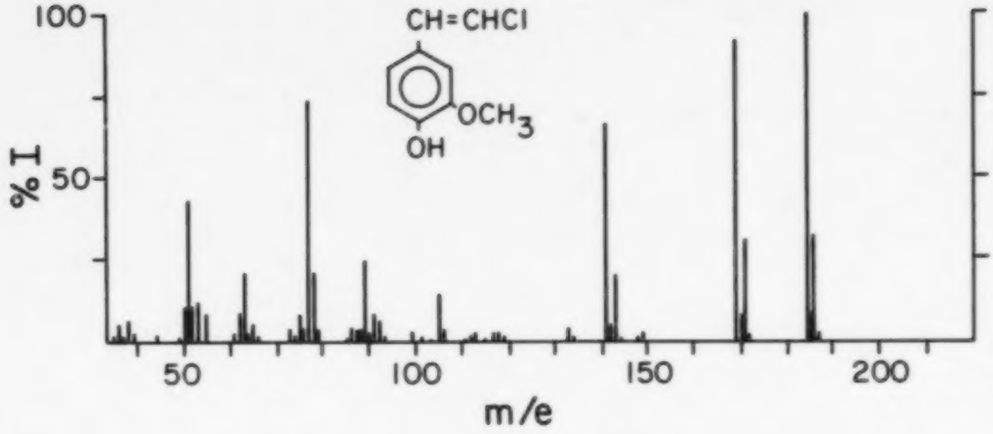

Figure B-54. Mass spectrum of β-chloro-3-methoxy-4-hydroxystyrene.

9-1/8"

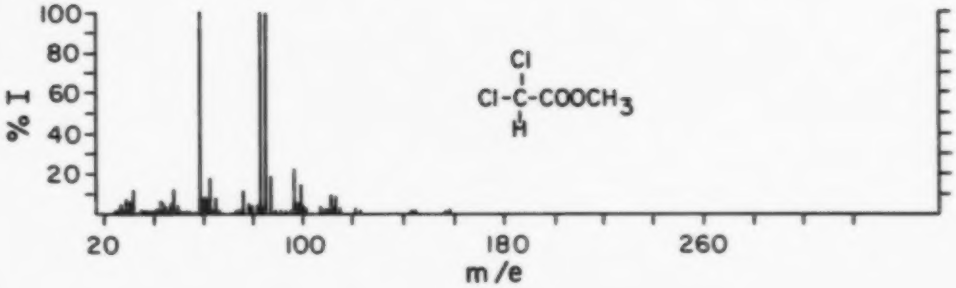

Figure B-55. Mass spectrum of dichloroacetic acid methyl ester.

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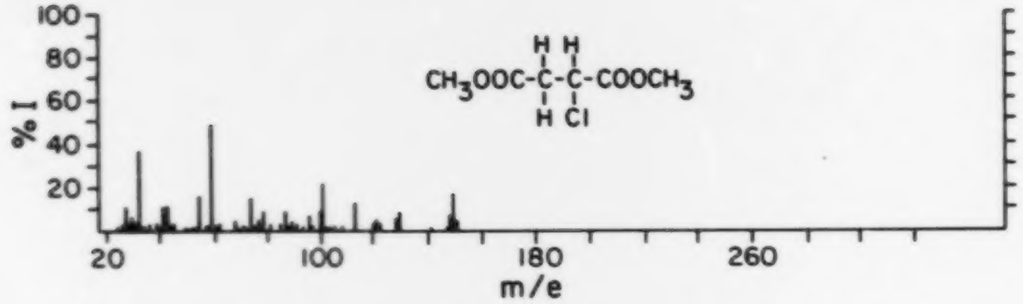

Figure B-56. Mass spectrum of chlorobutanoic acid dimethyl ester.

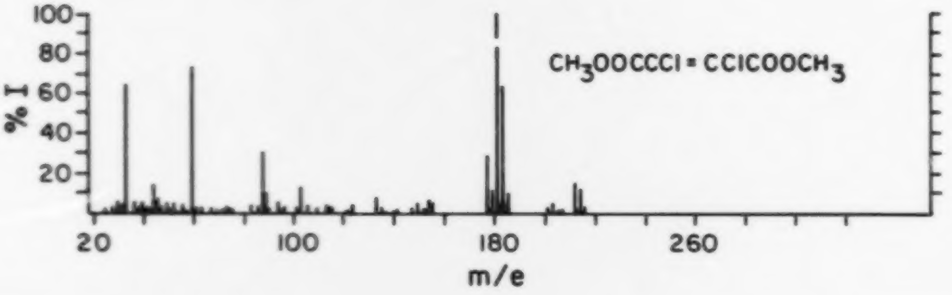

Figure B-57. Mass spectrum of dichlorobutenedioic acid dimethyl ester.

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APPENDIX C

REPRESENTATIVE TABULAR SPECTRA

This appendix contains a portion of the raw spectral data in tabular form, in particular the ether extract of chlorinated humic acid data from Table 22. It is included as an aid to those readers interested in the mass spectral interpretations made in this study. The identifying number of each proposed structure is given on the spectrum.

Definitions: (1) Mass - four decimal place accurate mass.

(2) % HT. MOD. - only ions above mass 40 are selected as base peaks, excluding air peaks.

Note: Spectra still contain background ions.

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BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
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EPA-287 (Cin.)
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PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.
1	25.0322	1.1	54	52.0351	0.7	107	91.0573	1.2
2	26.0393	3.5	55	53.0425	1.6	108	92.0022	0.8
3	27.0318	0.6	56	54.0377	1.8	109	92.0627	0.4
4	27.0344	0.9	57	55.0206	2.0	110	93.0154	0.6
5	27.0372	0.8	58	55.0554	4.2	111	100.0596	0.9
6	27.0472	26.5	59	56.0277	2.3	112	101.0621	1.9
7	28.0298	238.2	60	56.0543	7.2	113	110.9821	0.7
8	28.0547	13.0	61	57.0361	4.9	114	112.9779	0.9
9	29.0255	23.0	62	57.0727	35.0	115	115.0767	3.8
10	29.0621	52.1	63	58.0436	1.6	116	116.9072	0.9
11	30.0322	3.3	64	58.0743	2.4	117	118.9036	1.2
12	30.0652	1.4	65	59.0148	13.6	118	118.9926	1.8
13	31.0393	57.6	66	59.0503	24.0	120	127.9127	2.1
14	32.0099	93.1	67	60.0218	13.0	121	129.0924	0.9
15	32.0458	7.9	68	60.0538	1.5	122	130.9878	1.0
16	33.0467	0.5	69	60.9848	0.4	123	138.9045	2.8
17	33.0532	0.9	70	61.0297	6.3	124	150.9014	11.2
18	34.0118	0.9	71	61.9949	0.8	125	151.8963	0.6
19	34.9861	1.6	72	62.9638	0.9	126	168.9876	1.9
20	35.9938	2.2	73	62.9996	0.8	127	180.9868	0.9
21	36.9809	0.8	74	63.4515	1.2	128	230.9840	0.4
22	38.0166	1.7	75	63.9607	0.6	129	253.8090	7.9
23	38.0295	1.3	76	64.0105	0.7	130	265.3110	2.5
24	39.0188	0.8	77	68.9935	8.3	132	278.8128	2.2
25	39.0356	11.6	78	69.0325	3.1	134	405.6636	0.7
26	39.9747	8.5	79	69.0693	2.4	135	405.7269	1.1
27	40.0438	2.0	80	70.0408	3.1			
28	41.0160	1.6	81	71.0494	2.7			
29	41.0380	0.5	82	72.0571	5.1			
30	41.0515	38.6	83	72.9723	1.2			
31	42.0235	9.9	84	73.0283	2.1			
32	42.0592	3.8	85	73.0636	3.3			
33	43.0318	100.0	86	73.9786	21.9			
34	43.0683	14.9	87	74.0353	25.1			
35	44.0024	26.9	88	74.0713	6.0			
36	44.0380	14.5	89	74.9748	0.8			
37	44.0705	1.0	90	74.9811	0.8			
38	45.0100	17.1	91	74.9966	0.8			
39	45.0463	26.4	92	75.0044	0.6			
40	46.0167	4.6	93	75.0382	1.8			
41	46.0526	3.7	94	75.0480	0.6			
42	46.9732	8.1	95	75.9757	6.7			
43	47.0257	1.2	96	78.9963	0.8			
44	47.9862	3.8	97	81.9379	9.5			
45	48.9735	2.7	98	82.9462	4.1			
46	48.9921	2.6	99	83.9369	7.2			
47	49.9759	0.9	100	84.9457	2.9			
48	49.9805	0.8	101	85.0655	5.1			
49	49.9985	18.0	102	85.9344	1.3			
50	50.9871	0.7	103	86.0753	1.0			
51	51.0076	0.9	104	87.0453	2.0			
52	51.0260	1.1	105	87.0836	3.5			
53	51.9939	6.1	106	88.0543	9.3			

NUMBER 9

BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS

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6	28.0294	121.9	59	59.0153	30.8	112	102.0374	0.4
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11	30.0670	1.5	64	61.0293	7.5	117	110.9940	0.9
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13	32.0103	45.7	66	63.0006	12.1	120	127.9137	1.1
14	32.0459	3.6	67	63.4535	1.0	121	130.9855	1.1
15	33.0532	4.3	68	64.0061	3.5	122	146.9912	0.4
16	34.0127	0.4	69	64.9978	3.0	123	150.9044	5.3
17	34.9879	0.4	70	65.0146	0.3	124	151.9180	0.3
18	35.9930	0.7	71	66.0059	1.4	125	168.9901	1.3
19	37.0248	0.2	72	67.0593	0.4	126	180.9770	0.3
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21	38.0331	0.4	74	68.9952	4.3	128	253.0080	3.5
22	39.0371	2.4	75	69.0378	0.3	129	265.0079	1.3
23	39.9760	4.2	76	69.0692	1.9	131	278.0097	0.9
24	40.0427	0.6	77	70.0421	3.3	133	405.7175	0.8
25	40.0474	0.6	78	70.0757	0.4			
26	41.0166	1.4	79	71.0485	2.1			
27	41.0231	0.9	80	71.0861	0.4			
28	41.0530	7.1	81	72.0575	1.2			
29	42.0247	7.7	82	73.0294	1.9			
30	42.0605	1.4	83	73.0659	2.8			
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32	43.0667	5.6	85	74.0736	0.8			
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34	44.0037	9.7	87	75.9728	0.7			
35	44.0391	10.3	88	76.0074	0.3			
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37	45.0469	67.3	90	77.0166	1.1			
38	46.0178	1.6	91	77.9722	0.4			
39	46.0518	2.5	92	77.9865	0.4			
40	46.9768	0.5	93	78.9785	3.2			
41	47.0247	2.0	94	78.9995	0.3			
42	47.9863	0.7	95	79.0146	0.6			
43	48.9932	5.9	96	79.0215	0.3			
44	49.9989	4.7	97	82.0454	0.4			
45	50.9656	2.4	98	82.0807	0.3			
46	51.0016	0.3	99	83.0518	0.6			
47	51.0122	0.5	100	84.9425	0.3			
48	51.0286	0.7	101	85.0687	1.5			
49	51.9937	2.1	102	86.9664	0.8			
50	53.0428	1.0	103	87.0493	2.9			
51	54.0498	0.7	104	87.0861	0.9			
52	55.0210	2.4	105	88.0562	1.3			
53	55.0570	2.5	106	88.9841	0.6			

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BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
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3	26.0406	1.0	56	63.4526	1.0	110	130.9900	0.5
4	27.0482	3.7	57	63.9930	1.4	111	138.9050	0.9
5	28.0297	100.0	58	64.9602	0.5	112	141.9287	0.2
6	28.0543	0.9	59	64.9977	6.0	113	142.9688	0.4
7	29.0260	7.6	60	66.0037	0.4	114	143.9589	0.3
8	29.0626	1.0	61	68.9961	2.6	115	144.9544	0.3
9	30.0325	1.2	62	71.0857	0.2	116	150.9034	2.7
10	31.0394	5.6	63	73.0260	0.4	117	156.9863	0.5
11	32.0100	40.0	64	73.0652	0.7	118	158.9759	0.4
12	32.0464	1.2	65	74.0334	0.4	119	168.9813	0.4
13	33.0531	0.6	66	74.0403	0.4	120	253.8077	1.3
14	34.9862	1.4	67	75.9724	10.1	121	265.8172	0.3
15	35.9940	1.5	68	76.9772	0.8	123	278.8202	0.3
16	36.9822	0.5	69	77.0174	0.6	125	405.7354	0.3
17	37.9884	0.6	70	77.9694	3.8			
18	39.0378	0.3	71	78.9945	2.4			
19	39.9767	3.8	72	80.9937	1.0			
20	40.0086	0.5	73	81.9383	3.1			
21	41.0173	1.5	74	82.8932	0.2			
22	41.0535	0.8	75	82.9468	100.0			
23	42.0248	1.1	76	83.9438	2.6			
24	43.0327	5.3	77	84.9442	100.0			
25	43.0686	0.5	78	85.9454	1.4			
26	43.0747	0.3	79	86.9421	17.3			
27	44.0040	5.1	80	87.9430	0.3			
28	44.0399	0.7	81	88.9834	0.9			
29	45.0105	1.4	82	89.9924	0.6			
30	45.0474	2.8	83	90.9769	0.4			
31	46.0177	0.7	84	93.0119	0.9			
32	46.0520	0.3	85	95.0096	0.4			
33	46.9805	4.7	86	95.0210	0.4			
34	47.9869	11.3	87	95.9542	0.9			
35	48.9839	2.2	88	96.9632	20.2			
36	49.9806	3.6	89	97.9699	3.6			
37	49.9934	1.6	90	98.9603	13.5			
38	50.9867	0.7	91	99.9675	2.5			
39	51.0056	1.6	92	100.9569	2.2			
40	51.9949	0.7	93	101.9666	0.5			
41	53.0036	0.7	94	106.9920	2.3			
42	54.0143	0.2	95	108.9880	1.1			
43	55.0212	0.4	96	109.9355	1.6			
44	55.0582	0.5	97	110.9410	8.2			
45	57.0369	0.8	98	111.9310	1.1			
46	57.0737	0.3	99	111.9496	0.5			
47	57.0766	0.3	100	112.9395	6.1			
48	59.0148	100.0	101	113.9389	0.4			
49	59.0519	1.7	102	114.9433	1.1			
50	59.9773	0.7	103	118.9923	0.6			
51	60.0189	7.7	104	121.0937	2.0			
52	60.9866	7.7	105	123.0019	0.9			
53	61.0227	1.5	107	126.9470	0.2			

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3	26.0401	1.2	56	62.9975	0.5	110	131.9104	0.5
4	27.0480	5.4	57	63.4534	0.9	111	138.9006	1.1
5	28.0290	100.0	58	63.9626	0.3	112	140.9505	7.0
6	28.0542	2.6	59	63.9709	0.4	113	141.9553	0.3
7	29.0257	11.0	60	63.9893	0.2	114	142.9462	5.2
8	29.0621	24.2	61	64.9603	3.4	115	143.9571	0.3
9	30.0325	2.8	62	68.9951	2.4	116	144.9445	1.0
10	30.0618	0.4	63	69.0676	0.3	117	146.3045	0.3
11	30.0662	0.6	64	69.9706	0.4	118	150.9027	4.1
12	31.0394	4.1	65	73.9217	0.3	119	151.9134	0.2
13	32.0101	30.3	66	73.0298	0.4	120	168.9902	0.7
14	32.0453	0.9	67	73.0661	1.3	121	180.9881	0.5
15	33.0519	0.4	68	74.0370	0.5	122	218.9860	0.3
16	33.0576	0.3	69	75.9642	0.5	123	253.8077	3.1
17	34.9858	3.9	70	75.9739	0.7	124	265.8112	1.2
18	35.9935	2.0	71	76.9611	0.3	126	278.8150	0.8
19	36.9817	1.7	72	77.0148	1.1	128	405.7048	0.4
20	37.9081	0.6	73	77.9706	0.3			
21	39.0365	0.4	74	78.0467	0.3			
22	39.9751	3.5	75	79.0156	0.4			
23	40.0074	1.1	76	81.9388	26.0			
24	41.0165	0.4	77	82.9475	3.9			
25	41.0520	1.2	78	83.9382	15.1			
26	42.0248	0.4	79	84.9453	3.1			
27	43.0318	3.9	80	85.9344	3.2			
28	43.9687	0.5	81	86.9397	0.3			
29	44.0032	4.3	82	87.0478	0.4			
30	44.0428	0.4	83	90.0348	0.8			
31	45.0106	1.0	84	94.9470	0.5			
32	45.0470	2.4	85	95.9553	0.2			
33	46.0175	0.6	86	96.9594	1.9			
34	46.9803	21.5	87	98.9585	1.0			
35	47.9857	2.4	88	109.9345	2.2			
36	48.9773	7.2	89	110.9417	0.7			
37	49.9794	0.9	90	111.9308	1.2			
38	49.9991	1.3	91	112.9556	5.6			
39	50.9883	0.8	92	113.9320	0.6			
40	51.0184	0.6	93	114.9517	3.4			
41	51.9949	0.4	94	116.9053	42.6			
42	55.0583	0.8	95	116.9439	0.6			
43	55.9763	0.8	96	117.9138	0.6			
44	56.0632	0.3	97	118.9035	40.9			
45	56.9740	0.8	98	118.9917	0.9			
46	57.0366	0.3	99	119.9059	0.7			
47	58.0098	0.2	100	120.9000	11.7			
48	59.0144	100.0	101	121.9038	0.2			
49	59.0509	0.8	102	122.8970	1.2			
50	59.9767	0.7	103	124.9600	0.5			
51	60.0181	3.3	105	126.9556	0.3			
52	60.9864	4.5	106	127.9124	0.8			
53	61.0210	1.6	107	129.9165	0.6			

NUMBER 22*

BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
BEGIN LAST LINE OF TEXT
3/8"

EPA-287 (Cin.)
(4-76)

PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.
1	24.0250	4.2	54	86.9667	2.7
2	24.0273	5.5	55	94.9469	8.7
3	26.0409	2.2	56	96.9459	5.7
4	27.0439	4.0	57	107.9978	14.9
5	27.0478	6.0	58	108.9599	3.2
6	27.0516	5.7	59	109.9935	6.7
7	28.0234	*******	60	112.9544	3.2
8	28.0555	3.2	61	116.9050	14.1
9	29.0254	27.3	62	118.9016	15.9
10	29.0618	10.2	63	118.9683	12.2
11	30.0328	4.2	64	120.9020	5.7
12	31.0394	22.1	65	122.9381	100.0
13	32.0098	415.9	66	123.9355	4.2
14	32.0460	7.7	67	123.9497	4.5
15	34.0129	3.7	68	124.9353	60.3
16	35.9930	12.2	69	125.9359	3.2
17	37.9884	3.5	71	127.9075	5.5
18	39.0361	4.0	72	130.9888	6.7
19	39.0414	2.7	73	138.9018	10.9
20	39.9750	39.5	74	140.9484	6.9
21	41.0527	9.2	75	142.9556	2.0
22	42.0262	2.7	76	150.9039	59.3
23	43.0315	22.3	77	153.9573	12.7
24	43.0585	5.0	78	154.9606	2.0
25	44.0026	26.1	79	155.9522	10.2
26	44.0376	3.7	80	168.9876	8.9
27	45.0091	7.7	81	180.9859	4.2
28	45.0469	11.7	82	253.8111	30.0
29	46.9797	7.7	83	265.8110	13.6
30	47.9866	3.2	85	278.8215	7.9
31	48.9728	2.5	87	405.7059	5.2
32	48.9917	2.2			
33	49.9982	6.2			
34	51.9934	5.2			
35	55.0565	5.5			
36	56.0641	2.2			
37	59.0144	82.1			
38	59.0517	6.5			
39	59.9770	10.7			
40	60.0131	3.2			
41	60.0231	5.2			
42	61.0244	1.7			
43	61.9725	3.2			
44	61.9790	4.0			
45	62.9639	15.6			
46	63.4516	7.4			
47	64.9614	5.5			
48	69.9344	27.3			
49	73.0699	2.5			
50	81.9385	7.2			
51	82.9460	5.7			
52	83.9332	5.7			
53	84.9435	5.5			

NUMBER 22

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.
1	24.0250	1.5	54	71.0498	1.7
2	26.0413	3.5	55	73.0264	1.7
3	27.0482	11.0	56	73.0599	0.9
4	28.0302	430.6	57	74.0372	7.0
5	28.0428	4.3	58	78.9955	1.2
6	28.0551	9.6	59	82.0314	12.4
7	29.0265	8.8	60	83.0138	1.4
8	29.0619	5.4	61	83.0332	2.7
9	30.0331	1.4	62	83.0428	1.8
10	31.0399	6.0	63	85.0310	1.9
11	32.0105	177.4	64	86.0327	1.1
12	32.0472	2.6	65	86.0425	2.7
13	34.0128	1.4	66	87.0405	16.9
14	35.9933	3.6	67	88.0586	1.4
15	37.9895	1.9	68	101.0303	0.9
16	39.0312	0.7	69	101.0651	1.6
17	39.0356	1.7	70	103.0415	1.3
18	39.0399	2.6	71	113.0238	1.5
19	39.9758	15.5	72	114.0330	24.5
20	41.0382	0.8	73	115.0416	100.0
21	41.0529	6.2	74	116.0439	6.6
22	42.0250	4.9	75	117.0437	1.1
23	42.0461	1.2	76	118.9947	3.4
24	42.0496	1.5	78	127.9120	2.9
25	42.0553	1.5	79	130.9910	1.8
26	42.0619	2.0	80	138.9055	5.4
27	43.0323	10.0	81	150.9061	23.9
28	43.0684	3.0	82	168.9878	2.8
29	44.0028	8.4	83	169.0107	1.1
30	44.0386	1.9	84	180.9908	1.4
31	44.0426	0.7	85	253.9079	13.8
32	45.0104	2.5	86	265.8091	5.4
33	45.0469	10.4	88	278.8121	2.4
34	50.0011	2.2	90	405.7017	2.2
35	52.0247	1.7			
36	54.0388	14.6			
37	55.0242	53.4			
38	55.0596	1.3			
39	56.0277	4.3			
40	56.0657	1.3			
41	57.0377	5.2			
42	57.0712	1.8			
43	57.0775	1.2			
44	58.0452	1.6			
45	59.0153	50.1			
46	59.0463	1.7			
47	59.0540	2.2			
48	60.0209	3.0			
49	60.0275	1.2			
50	61.0349	1.8			
51	63.4537	3.7			
52	68.0510	4.5			
53	68.9965	8.1			

NUMBER 44

BEGIN LAST LINE OF TEXT

BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS

3/8"

PAGE NUMBER

EPA-287 (Cin.)
(4-76)

PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.
1	26.0377	0.7	54	63.4552	1.9	108	127.9776	0.6
2	26.0411	1.5	55	64.9985	1.1	109	128.9719	2.9
3	27.0483	4.6	56	65.0427	1.0	110	130.9721	0.7
4	28.0308	218.1	57	68.0515	0.6	111	130.9956	0.8
5	28.0554	1.1	58	68.9961	4.7	112	135.0476	1.7
6	29.0267	4.4	59	71.0509	0.7	113	136.0529	31.4
7	29.0626	1.9	60	73.0074	1.0	114	137.0569	3.4
8	30.0317	0.7	61	73.0655	0.7	115	138.9075	2.3
9	31.0400	2.2	62	74.0155	3.0	116	142.0663	0.6
10	32.0110	83.8	63	74.0351	1.0	117	143.0721	0.9
11	32.0472	0.7	64	75.0317	2.3	118	146.9907	0.6
12	33.0542	2.2	65	76.0310	3.7	119	149.0001	0.5
13	34.0112	0.7	66	76.9781	1.0	120	150.9069	11.2
14	35.9943	2.1	67	77.0392	60.3	121	151.9142	0.9
15	37.0273	0.6	68	77.9902	1.8	122	166.9945	1.4
16	37.9845	0.6	69	78.0445	4.8	123	180.9933	0.9
17	37.9897	1.1	70	79.9902	0.7	124	181.0146	0.5
18	38.0316	1.4	71	82.0314	1.8	125	253.8143	7.4
19	38.5336	1.1	72	82.9515	0.6	126	265.8243	2.7
20	39.0380	2.6	73	83.0122	0.4	127	269.0631	67.3
21	39.9770	8.7	74	83.0238	0.5	128	278.8205	1.7
22	41.0532	1.3	75	85.0347	0.9	130	405.6969	1.4
23	42.0250	0.7	76	87.0493	1.1			
24	43.0332	11.9	77	88.0569	1.1			
25	43.0690	1.0	78	88.9852	0.6			
26	44.0039	3.4	79	89.0277	2.9			
27	45.0094	1.3	80	89.9880	1.4			
28	45.0472	1.9	81	90.9984	2.4			
29	46.0152	0.4	82	91.0594	2.0			
30	48.9935	1.3	83	92.0067	0.7			
31	49.0152	0.8	84	92.0657	1.5			
32	49.0201	0.6	85	93.0021	0.6			
33	49.9989	0.6	86	93.0102	0.6			
34	50.0227	8.4	87	93.0218	0.4			
35	51.0099	0.7	88	95.0170	0.5			
36	51.0292	23.0	89	101.0649	2.7			
37	51.9971	0.7	90	103.0436	2.7			
38	52.0326	1.5	91	105.0386	100.0			
39	53.0091	0.8	92	106.0397	9.5			
40	54.0395	2.3	93	107.0430	0.5			
41	55.0226	1.6	94	107.0539	0.5			
42	55.0614	0.4	95	112.9635	0.7			
43	56.0300	1.0	96	113.0216	0.6			
44	57.0397	1.0	97	115.0290	0.4			
45	58.0432	1.0	98	115.0406	1.1			
46	59.0163	7.0	99	115.0740	0.9			
47	59.0514	1.5	100	118.9916	1.8			
48	60.0203	0.7	101	119.0073	0.7			
49	61.0325	0.9	102	120.0293	0.6			
50	61.9946	0.4	103	121.0101	2.5			
51	62.0143	0.5	104	122.9996	0.9			
52	63.0006	2.2	106	126.9739	4.2			
53	63.0248	0.8	107	127.9139	2.0			

NUMBER 52

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

PEAK NO.	MASS	%HT. MOD.
1	24.0256	4.5
2	26.0419	3.1
3	27.0486	4.8
4	28.0300	******
5	28.0454	2.6
6	28.0552	4.3
7	29.0266	26.1
8	29.0626	8.2
9	30.0328	4.3
10	31.0403	12.2
11	32.0107	472.2
12	32.0463	5.4
13	33.0547	4.3
14	34.0112	2.3
15	35.9940	11.6
16	37.9890	4.8
17	39.0382	6.0
18	39.9762	41.8
19	40.0317	2.6
20	41.0526	6.0
21	42.0240	2.6
22	42.0287	3.4
23	43.0322	17.0
24	43.0670	3.7
25	44.0037	16.8
26	45.0107	4.0
27	45.0471	7.1
28	48.9934	4.0
29	50.0007	2.8
30	51.0062	4.5
31	53.0076	9.4
32	54.0365	4.0
33	55.0205	6.0
34	55.0581	4.3
35	56.0275	3.7
36	58.0400	4.5
37	59.0151	43.7
38	59.9771	7.1
39	60.0175	2.6
40	61.9739	2.6
41	63.4521	8.0
42	68.9949	38.9
43	71.0104	2.6
44	73.0629	3.7
45	74.0353	4.0
46	78.9911	4.5
47	82.0308	7.4
48	82.9484	3.7
49	85.0315	4.0
50	86.9609	3.4
51	87.9723	4.3
52	88.9806	4.0
53	99.0476	3.1
54	100.0406	2.6
55	101.0314	3.4
56	118.9895	9.9
57	121.0007	4.0
59	127.9116	5.4
60	130.9919	4.8
61	138.9025	15.6
62	146.9834	100.0
63	147.9877	6.8
64	148.9811	31.5
65	149.9871	4.3
66	150.9026	65.1
67	168.9882	10.5
68	178.0006	6.5
69	180.9927	4.3
70	253.8098	42.0
71	265.8073	14.8
73	278.8135	11.6
75	405.7118	6.5

NUMBER 63

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.
1	24.0253	1.3	54	69.0334	1.3	108	150.9977	4.6
2	24.0271	1.0	55	69.0406	0.7	109	151.9161	0.8
3	26.0413	2.4	56	69.0646	0.8	110	168.9920	3.1
4	27.0475	10.0	57	69.0725	1.2	111	180.9885	1.7
5	28.0295	316.0	58	71.0132	1.9	112	253.8146	10.1
6	28.0543	1.3	59	72.0597	1.2	113	265.8126	3.2
7	28.0572	2.5	60	74.0364	14.2	114	276.9894	100.0
8	29.0267	6.6	61	75.0082	0.5	115	278.8248	2.9
9	29.0625	5.6	62	75.0428	1.2	117	405.7124	2.0
10	30.0333	0.8	63	75.9748	1.2			
11	31.0398	3.5	64	77.0153	4.7			
12	32.0106	128.4	65	78.9986	8.4			
13	33.0560	1.2	66	80.9935	3.2			
14	34.0145	1.0	67	85.0309	2.2			
15	35.9863	0.5	68	86.9611	0.7			
16	35.9939	3.2	69	86.9684	0.9			
17	37.9899	0.9	70	87.0472	8.0			
18	39.0378	3.2	71	88.0527	1.0			
19	39.9762	10.5	72	88.9841	3.6			
20	41.0527	11.0	73	90.9736	0.8			
21	42.0250	5.2	74	90.9941	2.2			
22	42.0605	1.8	75	92.9962	1.1			
23	43.0326	19.2	76	93.0078	0.7			
24	43.0687	2.7	77	96.0478	6.1			
25	43.0739	1.2	78	97.0323	1.7			
26	44.0039	5.4	79	100.0556	8.3			
27	45.0091	1.1	80	101.0622	21.8			
28	45.0469	3.3	81	102.0640	2.1			
29	48.9939	1.2	82	103.0298	0.7			
30	49.9988	1.2	83	103.0427	1.0			
31	51.0065	2.8	84	105.0338	1.8			
32	51.9951	0.8	85	106.0127	0.8			
33	53.0016	0.8	86	107.9976	2.1			
34	53.0109	1.1	87	113.0259	12.0			
35	54.0376	0.6	88	114.0257	0.9			
36	55.0221	15.6	89	118.9935	2.2			
37	55.0503	2.4	90	119.9990	2.8			
38	56.0242	1.1	91	121.0031	3.9			
39	56.0675	1.3	92	121.9940	0.8			
40	57.0371	1.8	93	122.9997	1.8			
41	57.0741	1.3	95	127.9121	2.1			
42	58.0355	0.7	96	128.0473	4.2			
43	58.0445	1.8	97	129.0549	7.1			
44	59.0160	48.0	98	130.0576	0.8			
45	59.0520	7.7	99	130.9922	1.2			
46	60.0200	2.2	100	138.9050	4.7			
47	60.9963	2.7	101	141.1217	1.1			
48	61.9932	3.0	102	146.9770	0.9			
49	62.9827	0.7	103	146.9910	1.3			
50	63.4524	2.7	104	147.9933	6.6			
51	63.9838	0.6	105	149.0006	17.1			
52	68.0500	4.3	106	149.9959	3.0			
53	68.9956	7.6	107	150.9042	16.0			

NUMBER 66

BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
BEGIN LAST LINE OF TEXT
3/8"
PAGE NUMBER

EPA-287 (Cin.)
(4-76)

PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.
1	26.0399	3.0	54	87.0412	2.0
2	27.9482	9.6	55	87.0494	3.8
3	28.0304	820.6	56	95.0098	2.8
4	28.0527	2.6	57	96.0508	5.0
5	28.0564	2.4	58	100.0543	3.6
6	29.0259	16.2	59	101.0626	4.2
7	29.0619	5.4	60	105.0369	4.6
8	31.0403	8.4	61	109.9334	4.8
9	32.0110	309.4	62	111.9269	2.6
10	32.0455	4.2	63	112.9574	11.4
11	34.0137	3.4	64	113.0235	2.4
12	35.9940	6.8	65	114.9513	7.6
13	37.9873	2.6	66	116.9458	2.2
14	37.9932	2.6	67	118.9932	4.6
15	39.0373	5.6	68	120.9998	1.4
16	39.9763	26.9	69	122.0346	3.4
17	41.0524	7.6	70	125.9638	7.4
18	42.0249	6.2	72	127.9133	6.4
19	43.0326	10.6	73	127.9582	6.2
20	44.0049	14.2	74	129.0490	3.0
21	45.0102	2.2	75	130.9853	2.6
22	45.0466	16.6	76	138.9043	6.6
23	46.9799	6.4	77	140.9498	28.3
24	48.9714	2.8	78	141.9397	1.4
25	48.9938	3.2	79	142.9474	17.8
26	55.0226	4.2	80	144.9432	4.6
27	55.0572	2.4	81	146.9814	2.2
28	59.0156	100.0	82	149.0010	3.8
29	59.0533	4.4	83	150.9038	41.7
30	60.0188	3.8	84	155.9741	12.8
31	60.9861	5.0	85	157.9595	5.6
32	61.9944	3.8	86	160.9535	2.4
33	62.9640	15.6	87	168.9884	8.6
34	63.4532	5.4	88	180.9861	3.0
35	64.9595	7.0	89	231.0028	1.4
36	64.9680	2.2	90	253.6119	27.1
37	68.0491	5.0	91	265.8118	10.6
38	68.0544	4.2	93	278.8182	6.6
39	68.9945	17.0	95	405.6992	5.0
40	69.0663	3.2			
41	73.0652	4.6			
42	74.0372	4.5			
43	74.9993	5.0			
44	75.9702	4.8			
45	76.9844	5.8			
46	77.0376	3.8			
47	77.9651	1.8			
48	78.9720	2.6			
49	79.9983	3.4			
50	81.9429	3.2			
51	82.9409	3.0			
52	82.9470	2.6			
53	84.9464	2.6			

NUMBER 69

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.
1	26.0414	5.4	54	74.9360	2.1	108	174.0151	3.1
2	27.0482	13.1	55	75.0004	3.7	109	176.0127	1.7
3	28.0299	853.1	56	75.0453	4.4	110	179.0081	4.6
4	28.0577	2.3	57	75.9933	2.3	111	180.9889	3.5
5	29.0264	20.2	58	78.0437	1.9	112	182.9606	9.0
6	29.0626	4.4	59	78.9977	1.9	113	184.9578	2.9
7	31.0397	10.0	60	82.9504	2.1	114	253.8091	40.2
8	32.0111	349.8	61	85.0317	13.5	115	265.8074	13.3
9	32.0475	2.5	62	88.9833	20.8	117	278.8135	8.1
10	33.0547	2.5	63	90.9813	7.3	119	405.7111	7.7
11	35.9934	9.8	64	95.9592	1.7			
12	37.0239	4.0	65	97.9622	1.7			
13	37.9894	4.4	66	101.0265	3.7			
14	38.0299	8.7	67	101.9908	6.0			
15	39.0380	20.8	68	102.9978	4.0			
16	39.9763	31.5	69	103.0393	4.4			
17	40.0446	2.3	70	103.9924	3.3			
18	40.0482	2.5	71	105.0128	13.3			
19	41.0537	8.7	72	105.0359	2.7			
20	42.0244	4.0	73	107.0110	6.7			
21	43.0322	16.0	74	110.9714	1.7			
22	43.0703	1.9	75	110.9842	2.3			
23	44.0042	13.5	76	112.9727	3.1			
24	44.0283	13.1	77	113.0276	5.0			
25	45.0105	2.7	78	115.0420	9.0			
26	45.0470	18.5	79	115.9781	6.2			
27	46.9814	2.5	80	117.0605	3.3			
28	47.0612	1.9	81	118.9698	4.6			
29	48.9937	4.0	82	118.9918	5.2			
30	49.9994	2.9	83	119.9994	4.6			
31	51.0088	2.5	84	125.0237	2.9			
32	53.0061	5.4	86	127.9114	6.0			
33	53.0135	3.3	87	130.9907	3.1			
34	53.0443	7.1	88	131.9990	14.0			
35	54.0170	1.9	89	133.0037	16.0			
36	55.0214	25.6	90	133.9952	8.3			
37	55.0612	2.7	91	135.0166	19.4			
38	56.0278	4.9	92	136.0210	2.3			
39	57.0376	3.1	93	137.0162	7.3			
40	59.0155	100.0	94	138.9042	13.1			
41	59.0521	25.2	95	143.0005	5.4			
42	60.0208	5.2	96	144.9978	2.5			
43	60.9856	8.7	97	146.9869	12.5			
44	61.0291	2.9	98	148.9827	6.0			
45	62.9802	1.9	99	150.9038	55.6			
46	63.4547	6.7	100	156.0405	13.1			
47	67.0183	7.3	101	157.0503	18.7			
48	68.0249	4.0	102	158.0601	1.7			
49	68.9948	28.1	103	159.9932	10.2			
50	69.0272	1.7	104	161.0021	21.0			
51	71.0125	3.1	105	161.9928	7.1			
52	72.9851	3.3	106	162.9922	7.5			
53	73.9948	2.5	107	168.9891	6.5			

NUMBER 84

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"
PAGE NUMBER

EPA-287 (Cin.)
(4-76)

PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.
1	24.0277	2.8	54	85.0376	1.3	108	206.8849	2.1
2	27.0459	3.3	55	86.9681	28.5	109	211.9666	15.3
3	28.0311	545.3	56	87.9708	2.0	110	212.9674	2.1
4	29.0269	11.5	57	88.0559	1.1	111	213.9647	11.3
5	29.0632	2.5	58	88.9672	9.9	112	215.9611	3.1
6	30.0348	2.0	59	89.9736	2.3	113	253.8068	23.0
7	31.0411	4.0	60	93.9423	5.5	114	265.8094	8.7
8	32.0114	221.6	61	94.9474	1.9	116	278.8112	5.3
9	35.9949	6.3	62	94.9561	2.0	118	405.7146	4.3
10	37.9908	3.5	63	95.9434	3.3			
11	39.0393	4.4	64	101.0276	2.7			
12	39.9773	10.5	65	101.0608	2.5			
13	41.0524	2.5	66	102.9639	12.3			
14	42.0239	2.0	67	104.9614	4.0			
15	42.0286	1.3	68	108.9631	2.0			
16	43.0328	13.3	69	109.9395	0.9			
17	43.0675	2.0	70	112.9631	3.2			
18	44.0043	8.5	71	114.0752	2.3			
19	44.0399	1.5	72	114.9558	2.3			
20	45.0117	3.1	73	115.0774	1.7			
21	45.0490	7.1	74	118.9949	4.3			
22	46.9810	4.0	75	120.9916	1.1			
23	48.9949	4.1	76	121.9293	1.6			
24	50.0028	2.1	77	121.9420	1.5			
25	51.0066	1.2	78	122.9437	2.4			
26	51.9998	3.9	80	127.9155	3.6			
27	54.0413	1.2	81	130.9978	1.7			
28	55.0228	2.0	82	133.0098	7.3			
29	55.0283	2.9	83	134.9995	3.1			
30	55.0604	2.3	84	136.9514	1.5			
31	56.0315	1.2	85	138.9051	8.5			
32	57.0367	1.5	86	138.9604	1.2			
33	58.9718	3.6	87	141.0563	1.7			
34	59.0165	72.4	88	146.9917	2.7			
35	59.0524	4.1	89	149.0020	5.2			
36	60.0200	2.3	90	150.9048	35.3			
37	60.9663	1.5	91	150.9906	1.9			
38	60.9728	1.2	92	151.9025	1.7			
39	60.9861	1.9	93	151.9158	1.5			
40	61.0343	1.2	94	152.9534	5.9			
41	62.9652	2.7	95	154.9478	4.8			
42	62.9718	2.4	96	168.9912	5.7			
43	63.4554	3.9	97	176.9969	27.7			
44	67.0588	1.7	98	178.0059	2.5			
45	68.9972	12.5	99	178.9949	12.0			
46	69.0374	1.2	100	180.9470	100.0			
47	71.0544	2.0	101	181.9518	5.5			
48	72.9860	2.0	102	182.9442	63.1			
49	73.0674	2.7	103	183.9528	3.9			
50	74.0372	1.9	104	184.9410	10.0			
51	74.9609	1.5	105	200.9227	2.3			
52	82.9504	3.9	106	202.9266	4.1			
53	84.9475	3.1	107	204.8684	1.6			

NUMBER 96

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.
1	24.0277	2.6	54	64.9625	2.8	108	133.9980	11.8
2	26.0406	4.7	55	67.0185	7.3	109	134.9934	13.4
3	27.0466	28.3	56	68.0210	2.3	110	136.9997	16.3
4	28.0308	712.2	57	68.9972	24.7	111	138.9046	12.3
5	28.0560	3.3	58	69.0340	4.0	112	138.9946	9.7
6	29.0270	25.0	59	71.0135	2.4	113	140.9989	3.0
7	29.0630	3.8	60	71.0497	2.1	114	146.9844	3.0
8	30.0294	1.4	61	72.0220	3.3	115	150.9047	43.5
9	30.0350	3.3	62	72.9840	6.3	116	156.0442	43.5
10	31.0400	8.3	63	73.0644	3.1	117	157.0503	45.2
11	32.0112	310.1	64	73.9916	4.5	118	158.0554	6.4
12	33.0546	1.9	65	74.0360	3.5	119	159.0343	2.3
13	34.0100	1.4	66	74.9988	5.0	120	159.9913	20.3
14	34.0139	2.6	67	75.0453	5.2	121	161.0003	30.1
15	35.9944	9.0	68	75.9739	3.3	122	161.9924	9.6
16	37.0211	1.9	69	75.9933	2.8	123	162.9962	12.5
17	37.0249	3.5	70	76.9759	3.3	124	164.0110	2.3
18	37.9908	2.6	71	76.9834	2.4	125	168.9873	7.0
19	38.0310	8.3	72	76.9935	2.1	126	170.0083	3.3
20	39.0384	31.7	73	78.9778	2.6	127	180.9531	4.2
21	39.9770	28.3	74	78.9966	7.8	128	182.9363	3.3
22	40.0453	3.1	75	83.0167	3.3	129	253.8049	30.1
23	41.0165	3.8	76	85.0327	3.0	130	265.8059	12.2
24	41.0538	9.7	77	87.0445	2.8	132	276.8072	7.1
25	42.0244	5.7	78	88.0602	2.3	134	405.7157	4.0
26	43.0337	15.8	79	88.9809	4.7			
27	44.0046	10.4	80	89.0173	3.0			
28	45.0102	3.3	81	98.0415	3.0			
29	45.0152	2.3	82	101.0267	2.1			
30	45.0491	13.6	83	101.0675	3.1			
31	46.9805	4.0	84	101.9920	12.5			
32	47.0620	2.3	85	102.9632	2.3			
33	47.9867	2.4	86	102.9975	4.2			
34	48.9940	5.7	87	103.0426	6.1			
35	50.9857	2.1	88	103.9898	2.4			
36	50.9910	1.6	89	105.0133	24.9			
37	51.0067	5.2	90	106.0205	1.9			
38	53.0438	7.8	91	107.0075	9.9			
39	54.0401	1.9	92	108.9890	1.7			
40	55.0225	38.4	93	109.0064	3.7			
41	55.0443	3.3	94	113.0251	5.7			
42	55.0537	1.9	95	113.0604	2.3			
43	55.0605	3.0	96	115.0389	3.3			
44	56.0250	2.6	97	116.9772	11.7			
45	57.0362	4.5	98	117.9841	1.7			
46	57.0757	2.3	99	118.9861	7.3			
47	59.0167	100.0	100	125.0249	7.7			
48	59.0541	3.0	102	127.9141	7.0			
49	60.0134	4.7	103	128.9715	2.4			
50	60.9364	5.7	104	129.0545	3.3			
51	62.9640	8.2	105	131.0341	9.6			
52	62.9942	3.1	106	131.9981	37.4			
53	63.4545	5.2	107	133.0057	21.4			

NUMBER 100

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"
PAGE NUMBER
EPA-287 (Cin.)
(4-76)

PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.
1	24.0281	5.1	54	100.0008	7.0
2	26.0404	4.0	55	101.0653	3.7
3	27.0487	10.3	56	103.0389	7.3
4	28.0300	******	57	103.0472	2.6
5	28.0555	6.6	58	107.9971	5.9
6	29.0264	31.5	59	115.0410	6.2
7	29.0624	16.5	60	116.0507	11.0
8	31.0392	10.6	61	118.9917	9.9
9	32.0107	603.7	63	127.9146	9.9
10	33.0546	3.7	64	135.9674	7.7
11	34.0137	6.2	65	137.0098	2.9
12	34.9867	3.3	66	138.9042	22.3
13	35.9935	16.5	67	138.9923	4.0
14	37.9871	4.4	68	143.0350	5.1
15	37.9909	4.0	69	146.9765	3.7
16	39.0373	14.7	70	146.9892	7.7
17	39.9765	61.2	71	150.9050	100.0
18	41.0405	5.9	72	151.0226	3.3
19	41.0531	11.0	73	151.9056	3.7
20	43.0325	37.7	74	168.9894	13.6
21	43.0686	8.4	75	253.8106	64.1
22	44.0039	18.7	76	265.8082	21.2
23	44.0391	4.8	79	278.8107	16.1
24	45.0084	4.4	80	405.7179	10.3
25	45.0466	16.5			
26	49.9940	8.4			
27	50.9868	6.2			
28	54.0348	4.8			
29	54.0393	5.5			
30	54.0445	4.0			
31	55.0234	9.2			
32	55.0465	53.8			
33	57.0351	5.5			
34	57.0405	5.5			
35	57.0737	6.2			
36	59.0157	52.7			
37	59.0520	6.2			
38	60.9864	7.7			
39	61.0306	5.9			
40	63.4535	13.2			
41	66.0325	4.8			
42	66.0400	5.9			
43	68.9947	30.8			
44	69.0713	9.2			
45	71.0112	3.3			
46	73.0638	7.0			
47	74.0369	23.8			
48	75.0452	5.5			
49	82.9490	6.6			
50	83.0525	3.3			
51	87.0472	19.8			
52	88.9778	4.0			
53	99.9891	4.0			

NUMBER 115

BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
BEGIN LAST LINE OF TEXT
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.
1	27.0481	15.7	54	124.0527	7.5
2	28.0299	******	55	125.0158	11.0
3	28.0554	9.8	56	125.0591	13.4
4	29.0261	26.4	57	126.0257	4.3
5	29.0620	18.1	59	127.0070	5.5
6	31.0397	11.4	60	127.9089	12.2
7	32.0104	674.8	61	128.0795	9.8
8	35.9924	15.0	62	130.9975	3.9
9	37.0243	13.0	63	138.9018	20.9
10	37.9907	3.9	64	146.9888	5.5
11	39.0366	11.0	65	149.0561	9.8
12	39.3757	73.6	66	150.9033	100.0
13	40.0444	5.1	67	151.9074	3.5
14	41.0519	21.7	68	157.0255	17.3
15	42.0246.	[illegible].7	69	168.9878	16.5
16	42.0598	8.3	70	180.9939	7.5
17	43.0317	39.0	71	230.9904	5.5
18	43.0695	13.8	72	253.8111	67.3
19	44.0028	19.7	73	265.8107	25.2
20	45.0461	11.4	75	278.8163	14.2
21	49.0448	4.7	77	405.7165	10.2
22	54.0486	3.5			
23	55.0206	13.8			
24	55.0571	22.4			
25	56.0253	3.1			
26	57.0356	8.7			
27	57.0707	13.0			
28	59.0152	33.5			
29	59.0527	9.1			
30	63.4521	15.7			
31	68.0610	7.9			
32	68.9951	40.2			
33	69.0398	3.5			
34	69.0698	23.6			
35	72.0806	5.9			
36	73.0648	16.9			
37	74.0345	31.5			
38	75.0439	5.1			
39	83.0504	16.1			
40	85.0311	18.1			
41	87.0484	12.6			
42	87.0842	9.1			
43	89.0404	2.8			
44	96.0563	5.9			
45	97.0701	10.2			
46	100.0545	5.9			
47	101.0328	5.9			
48	101.0638	4.7			
49	103.0395	7.1			
50	111.0829	4.3			
51	114.0323	4.3			
52	115.0761	37.8			
53	118.9908	8.3			

NUMBER 120

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

EPA-287 (Cin.)
(4-76)

PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.
2	27.0494	1.5	83	108.9460	3.4
3	28.0298	271.0	86	112.9586	3.6
4	29.0260	5.3	87	114.9563	2.2
5	29.0626	1.5	88	115.0772	1.3
6	31.0402	1.9	89	118.9987	1.5
7	32.0107	110.4	90	120.0209	2.8
8	32.0475	1.2	95	127.9140	2.6
12	35.9945	3.0	97	132.0166	1.1
14	37.9891	2.3	98	133.0249	3.2
15	38.0320	1.1	100	135.0436	6.5
16	39.0381	2.8	102	136.0540	1.3
17	39.9762	10.1	103	138.9039	3.6
18	41.0533	2.8	107	146.9777	1.2
19	43.0329	4.8	108	146.9905	2.0
20	44.0032	3.6	109	150.0183	1.5
21	45.0471	2.8	110	150.0746	15.6
23	50.0222	5.0	113	156.9533	1.1
24	51.0089	1.1	114	158.9354	1.3
25	51.0163	1.2	116	163.0415	100.0
26	51.0287	3.8	117	164.0437	11.6
27	52.0192	1.9	118	165.0454	1.7
28	53.0077	1.4	119	168.9895	2.5
29	55.0238	1.5	121	170.9198	1.3
30	55.0566	1.9	122	172.9128	1.1
31	57.0411	1.3	124	180.9779	1.4
32	57.0727	1.5	126	182.9773	1.3
33	59.0155	19.3	127	194.0579	6.6
34	59.0511	2.3	129	196.9810	1.5
37	63.0236	1.2	131	200.9289	6.2
38	63.4546	2.4	133	202.9250	6.6
39	64.0306	2.2	135	204.9231	2.1
40	65.0408	1.1	137	224.9770	6.2
41	66.0121	2.9	139	226.9691	3.7
43	68.9958	5.8	140	228.9251	2.1
45	69.0685	1.1	144	230.9198	3.2
48	71.9764	3.2	146	253.8095	11.4
50	73.0648	1.8	147	265.8095	4.3
51	74.0138	1.7	149	278.8095	2.3
53	74.0375	2.0			
55	75.0255	2.1			
57	76.0317	7.1			
58	77.0405	13.6			
59	78.0419	2.3			
60	78.9962	10.3			
61	79.0558	1.3			
62	80.9938	4.2			
66	86.9657	1.3			
70	91.0596	1.2			
71	92.0306	6.6			
76	103.0031	1.7			
77	104.0284	4.6			
78	105.0329	3.3			
80	105.9484	3.3			

NUMBER 159

BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
BEGIN LAST LINE OF TEXT
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.
1	24.0276	3.5	54	87.9973	3.9
2	27.0486	12.1	55	88.0457	4.3
3	28.0304	******	56	88.0548	5.5
4	29.0267	30.9	57	103.0405	5.1
5	29.0632	11.7	58	118.9951	16.0
6	30.0332	5.9	59	120.0192	4.3
7	31.0399	10.5	61	127.9143	9.0
8	31.0439	4.3	62	129.0858	5.1
9	32.0109	623.0	63	130.9902	5.5
10	34.0162	5.9	64	135.0414	13.7
11	35.9940	16.4	65	135.0602	7.4
12	37.9863	8.2	66	138.9044	25.0
13	37.9924	4.3	67	143.1072	6.6
14	39.0367	10.9	68	146.9857	6.6
15	39.9762	53.9	69	150.9023	100.0
16	41.0535	17.6	70	151.9170	5.1
17	42.0243	4.3	71	158.9611	5.5
18	42.0613	7.4	72	158.9819	7.0
19	43.0332	25.8	73	160.9742	4.7
20	43.0690	17.2	74	163.0374	63.3
21	44.0039	21.9	75	164.0420	10.2
22	44.0350	3.9	76	168.9901	13.7
23	45.0471	13.7	77	173.0356	4.3
24	50.0256	6.6	78	180.9928	3.9
25	52.0210	4.3	79	183.0199	6.6
26	53.0513	4.3	80	184.0105	4.7
27	55.0198	8.2	81	185.1515	3.1
28	55.0580	16.9	82	187.9221	4.3
29	56.0649	6.6	83	189.9156	2.7
30	57.0402	5.1	84	194.0579	13.3
31	57.0720	15.6	85	197.1943	2.7
32	58.0435	5.9	86	218.9869	5.1
33	59.0142	57.0	87	220.9391	7.8
34	59.0486	5.9	88	222.9332	4.3
35	59.0559	8.2	89	253.8055	64.5
36	63.4540	18.7	90	265.8116	25.8
37	67.0543	5.1	92	278.8114	18.0
38	68.9951	27.3	94	405.7115	10.5
39	69.0348	5.9			
40	69.0730	13.3			
41	71.0491	6.2			
42	71.0865	5.1			
43	73.0651	13.3			
44	74.0371	59.4			
45	75.0392	10.9			
46	76.0360	4.7			
47	77.0388	5.5			
48	81.0725	5.5			
49	83.0922	5.1			
50	85.0330	5.1			
51	85.0677	8.2			
52	86.1010	12.1			
53	87.0481	32.4			

NUMBER 163

BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
BEGIN LAST LINE OF TEXT
3/8"
PAGE NUMBER
EPA-287 (Cin.)
(4-76)

PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.
1	24.0268	5.5	54	87.0476	14.3	108	226.9722	4.9
2	27.0455	5.2	55	88.0524	5.5	109	253.8045	56.0
3	27.0487	10.1	56	92.0258	3.3	110	265.8131	21.2
4	28.0304	******	57	95.0880	2.9	112	278.8121	12.7
5	28.0557	5.2	58	96.9958	3.6			
6	29.0267	28.7	59	97.0716	6.8			
7	29.0629	10.7	60	97.1046	9.1			
8	31.0403	8.5	61	98.0753	5.5			
9	32.0101	541.7	62	98.0875	3.6			
10	35.9943	13.0	63	99.0431	3.9			
11	37.9889	6.2	64	101.0302	3.6			
12	39.0380	7.5	65	101.0651	12.7			
13	39.9762	52.4	66	103.0248	9.1			
14	41.0517	17.3	67	104.0288	4.9			
15	42.0256	3.6	68	107.0537	3.6			
16	42.0588	6.5	69	107.0860	2.9			
17	43.0322	40.1	70	110.0792	2.9			
18	43.0682	10.7	71	111.0838	14.7			
19	44.0034	19.9	72	112.0896	3.6			
20	44.0399	3.9	73	113.0697	2.9			
21	45.0467	9.4	74	115.0319	3.6			
22	50.0226	6.5	75	115.0438	3.3			
23	52.0176	4.2	76	119.0010	8.8			
24	53.0447	4.9	77	120.0186	6.8			
25	55.0210	13.0	78	124.0892	7.8			
26	55.0575	22.8	79	125.0917	7.8			
27	56.0626	6.8	80	125.1059	4.9			
28	57.0349	7.2	82	127.9147	11.4			
29	57.0719	7.5	83	128.0837	3.6			
30	59.0150	37.8	84	130.9947	4.6			
31	59.0533	8.1	65	135.0467	27.0			
32	63.4543	10.1	86	136.0501	5.5			
33	66.0105	10.1	87	137.0429	2.3			
34	67.0112	4.2	88	138.9045	17.9			
35	67.0528	6.8	89	143.1086	11.7			
36	67.0604	6.5	90	146.9895	5.2			
37	68.0586	4.9	91	150.9040	85.7			
38	68.9947	19.9	92	151.9104	3.9			
39	69.0377	3.3	93	152.0844	21.8			
40	69.0704	16.3	94	153.0931	3.9			
41	70.0719	4.9	95	163.0402	100.0			
42	71.0836	3.6	96	164.0442	15.0			
43	73.0655	6.2	97	166.9644	4.9			
44	74.0373	31.9	98	167.0478	6.8			
45	75.0236	7.5	99	156.9908	12.1			
46	75.0445	5.5	100	169.9891	2.9			
47	76.0309	10.1	101	180.9993	2.9			
48	77.0375	10.7	102	185.1201	12.7			
49	81.0747	5.5	103	194.0618	26.4			
50	83.0522	5.5	104	200.9359	4.9			
51	83.0880	10.2	105	202.9150	2.9			
52	84.0619	10.4	106	202.9412	2.9			
53	85.0347	4.6	107	224.9797	4.9			

NUMBER 168

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.
1	27.0476	8.6	54	86.9674	15.2	108	265.8123	30.0
2	27.0522	6.6	55	87.0429	6.6	109	270.9362	10.1
3	28.0304	******	56	88.9574	6.2	110	272.9361	10.1
4	29.0264	28.9	57	93.9416	3.9	111	274.9269	7.8
5	29.0315	5.4	58	97.0718	6.2	112	276.9161	3.9
6	29.0620	13.2	59	101.0627	5.1	114	278.8159	11.3
7	29.0662	7.0	60	102.9638	6.6	116	405.7108	10.9
8	31.0404	8.9	61	103.0405	8.2	117	405.7836	5.1
9	32.0109	689.5	62	109.0059	21.4			
10	35.9941	18.3	63	109.0259	4.3			
11	37.9888	5.4	64	111.0025	9.3			
12	39.0373	7.4	65	112.9547	9.3			
13	39.9769	62.3	66	114.9572	10.1			
14	41.0541	14.4	67	116.9112	8.2			
15	42.0632	5.8	68	118.9044	8.6			
16	43.0323	33.1	69	118.9874	9.3			
17	43.0690	14.0	70	119.0004	6.2			
18	44.0043	22.6	71	121.9327	5.4			
19	45.0472	11.3	73	127.0454	10.5			
20	46.9818	3.9	74	127.9139	16.7			
21	51.0096	4.3	75	129.0915	3.5			
22	51.0278	3.1	76	137.0002	42.8			
23	55.0216	7.4	77	138.9040	28.4			
24	55.0587	11.7	78	138.9981	12.8			
25	56.0662	4.7	79	141.9273	4.3			
26	57.0370	8.9	80	146.9851	6.6			
27	57.0726	9.7	81	147.0075	5.8			
28	57.0781	5.4	82	148.9928	10.5			
29	59.0159	93.4	83	149.0135	7.4			
30	59.0533	9.7	84	150.9040	100.0			
31	60.0200	5.8	85	151.9068	2.7			
32	60.9841	3.5	86	152.9538	10.5			
33	62.9647	17.1	87	154.9469	3.9			
34	63.4546	9.3	88	156.9079	4.3			
35	64.9615	5.8	89	158.9001	7.4			
36	67.0530	3.9	90	164.9599	4.3			
37	68.9962	34.6	91	165.0043	2.7			
38	69.0362	3.5	92	168.9912	19.1			
39	69.0705	8.2	93	177.0571	5.1			
40	71.0133	5.4	94	180.9459	11.3			
41	71.0506	5.1	95	180.9842	7.4			
42	72.9800	5.8	96	182.9447	7.8			
43	73.0642	10.5	97	186.9752	6.6			
44	74.0365	15.6	98	193.0030	4.7			
45	75.0493	5.4	99	197.9740	2.7			
46	78.0474	5.8	100	198.0006	8.2			
47	78.9961	3.1	101	215.0536	3.5			
48	81.0737	7.8	102	215.0759	5.1			
49	82.9474	2.7	103	219.9827	5.1			
50	83.0828	5.4	104	220.9949	3.5			
51	83.0959	3.1	105	236.9632	4.3			
52	84.0599	4.3	106	248.9298	4.7			
53	85.0353	5.1	107	253.8075	70.8			

NUMBER 187

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-70)

PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.
1	24.0261	2.5	54	109.0084	10.7	109	292.9019	4.2
2	27.0488	6.5	55	109.1028	2.3	111	405.7079	4.6
3	28.0304	856.7	56	109.9292	5.4			
4	29.0261	14.9	57	109.9401	3.1			
5	29.0618	6.3	58	111.0077	11.5			
6	31.0394	5.9	59	111.9282	1.9			
7	32.0090	354.6	60	112.9445	3.1			
8	32.0131	354.6	61	112.9602	4.0			
9	35.9937	9.8	62	114.9532	3.3			
10	37.9885	4.2	63	115.9620	3.1			
11	39.0375	7.9	64	116.9048	2.3			
12	39.9763	26.6	65	118.9081	4.2			
13	41.0541	9.4	66	118.9835	5.0			
14	43.0323	14.4	67	118.9941	3.1			
15	43.0681	6.9	68	119.0034	3.3			
16	44.0035	13.4	70	127.9133	7.1			
17	45.0479	6.5	71	133.0046	4.4			
18	46.9828	2.5	72	136.9540	1.9			
19	48.9921	1.9	73	136.9973	6.7			
20	50.0223	1.9	74	138.9026	12.1			
21	51.0100	2.1	75	140.9056	3.1			
22	51.9993	2.9	76	142.8967	2.9			
23	53.0428	5.2	77	142.9094	2.9			
24	55.0228	4.0	78	146.9858	3.3			
25	55.0593	10.3	79	150.9048	55.0			
26	56.0659	2.5	80	151.9048	2.7			
27	57.0386	2.7	81	153.0176	1.9			
28	57.0747	5.2	82	161.0043	2.7			
29	59.0151	58.4	83	168.9867	9.0			
30	59.0551	2.1	84	180.9491	4.6			
31	60.0170	5.0	85	180.9871	1.7			
32	62.9677	2.7	86	182.9539	3.1			
33	63.4518	5.2	87	184.8955	2.5			
34	68.9946	16.3	88	185.9197	2.1			
35	69.0676	5.4	89	192.9370	2.7			
36	71.0508	2.3	90	192.9719	1.9			
37	71.0851	2.3	91	204.9872	100.0			
38	73.0654	3.3	92	205.9918	11.9			
39	74.0380	16.1	93	206.9868	33.9			
40	79.0515	3.1	94	207.9935	4.4			
41	81.9404	4.4	95	218.9938	1.9			
42	83.0199	4.2	96	220.9285	1.7			
43	83.0881	3.3	97	242.9427	1.9			
44	83.9380	2.3	98	253.8065	36.6			
45	85.0273	2.3	99	255.9098	4.0			
46	86.9662	29.9	100	257.9037	3.3			
47	87.0475	5.6	101	262.8805	4.2			
48	87.9724	2.1	102	264.8763	5.0			
49	88.0546	2.3	103	265.8092	14.9			
50	88.9639	9.0	104	266.8837	1.9			
51	101.0668	2.1	106	278.8190	7.7			
52	103.0395	5.0	107	290.8750	3.8			
53	107.9360	1.7	108	292.8768	3.8			

NUMBER 198

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"
PAGE NUMBER

EPA-287 (Cin.)
(4-76)

PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.
1	24.0254	0.8	54	73.0635	2.5	108	138.9051	5.7
2	26.0422	1.6	55	74.0361	100.0	109	139.1130	1.3
3	27.0482	4.5	56	75.0437	19.5	110	143.1073	10.9
4	28.0302	424.4	57	77.0377	0.9	111	144.1152	1.5
5	28.0559	1.7	58	78.0458	1.5	112	146.9602	2.8
6	29.0266	7.7	59	78.0531	0.9	113	150.9060	25.6
7	29.0621	12.4	60	79.0553	1.9	114	151.9058	1.0
8	31.0392	1.9	61	80.0682	0.9	115	153.0299	3.7
9	32.0100	171.3	62	81.0347	0.7	116	157.1283	1.8
10	32.0461	1.3	63	81.0719	3.7	117	163.0308	1.1
11	34.0128	1.6	64	82.0426	1.2	118	167.0489	13.2
12	35.9934	4.7	65	82.0798	3.2	119	168.0491	2.0
13	37.9875	2.0	66	83.0508	2.4	120	168.9935	4.4
14	37.9927	1.2	67	83.0884	9.6	121	171.1392	3.2
15	39.0378	4.6	68	84.0585	4.4	122	185.1580	2.8
16	39.9763	15.6	69	84.0914	2.0	123	198.0613	2.0
17	40.0426	0.9	70	85.0662	1.3	124	199.1748	3.3
18	40.0461	0.9	71	85.1034	3.6	125	203.0151	0.8
19	41.0531	20.8	72	86.9618	1.8	126	213.1926	1.3
20	42.0250	2.2	73	87.0469	67.2	127	218.9741	0.9
21	42.0300	1.5	74	88.0549	5.3	128	227.2003	6.8
22	42.0564	4.6	75	95.0560	1.1	129	228.2024	1.9
23	43.0321	14.6	76	95.0889	3.8	130	239.2393	4.6
24	43.0682	26.7	77	96.0529	1.0	131	241.2147	1.6
25	44.0039	5.6	78	96.0629	1.7	132	253.8096	14.5
26	44.0377	2.3	79	96.0919	1.8	133	265.8116	6.8
27	45.0479	6.2	80	96.1035	1.1	134	270.2578	7.0
28	51.0288	0.8	81	97.0701	5.9	135	271.2573	1.6
29	52.0225	0.8	82	97.1044	4.7	137	276.8115	3.4
30	53.0056	1.6	83	98.0756	2.7	138	334.9974	1.0
31	53.0439	2.9	84	99.1230	1.3	140	405.7009	2.3
32	54.0508	3.4	85	101.0634	5.8			
33	55.0223	5.1	86	102.0699	1.6			
34	55.0591	19.7	87	103.0409	16.9			
35	56.0653	6.5	88	104.0431	1.2			
36	57.0365	3.2	89	104.0525	0.9			
37	57.0729	14.9	90	107.0881	0.9			
38	58.0391	1.0	91	109.1029	2.0			
39	58.0480	1.6	92	111.0811	1.3			
40	59.0155	9.2	93	111.1189	1.8			
41	59.0524	4.5	94	114.0652	1.0			
42	61.0309	3.4	95	115.0389	1.0			
43	63.4535	2.7	96	115.0740	2.3			
44	67.0555	4.5	97	117.0519	1.3			
45	68.0625	2.4	98	118.9929	2.8			
46	68.9955	8.1	99	120.9938	1.0			
47	69.0316	1.3	100	125.0985	1.6			
48	69.0701	12.0	102	127.9110	5.7			
49	70.0386	1.2	103	129.0940	5.4			
50	70.0776	3.3	104	130.1035	1.3			
51	71.0127	4.6	105	130.9925	1.0			
52	71.0524	2.0	106	131.0043	1.2			
53	71.0858	7.3	107	137.0372	5.6			

NUMBER 230

BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
BEGIN LAST LINE OF TEXT
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.
1	24.0268	0.3	54	67.0521	0.4	107	120.0211	2.3
2	24.0299	0.2	55	67.0586	0.4	108	121.0210	0.4
3	27.0480	0.7	56	68.9966	1.7	109	122.0405	0.4
4	28.0300	100.0	57	69.0724	1.0	110	125.0979	0.4
5	29.0264	2.5	58	70.0799	0.3	112	127.9121	2.1
6	29.0629	0.8	59	71.0458	0.2	113	131.0074	0.5
7	30.0290	0.2	60	71.0847	0.3	114	132.0110	0.3
8	30.0322	0.3	61	73.0043	0.6	115	132.0226	0.4
9	30.0355	0.5	62	73.0139	0.3	116	133.0280	0.9
10	31.0399	0.7	63	73.0316	0.3	117	134.0376	2.0
11	32.0102	37.6	64	73.0653	0.5	118	135.0439	5.0
12	32.0484	0.3	65	74.0210	3.5	119	136.0428	0.5
13	35.9935	1.2	66	75.0239	8.1	120	137.0581	0.2
14	37.0245	0.3	67	75.0505	0.2	121	138.9037	1.1
15	37.5226	0.2	68	76.0317	5.1	122	141.9419	0.3
16	37.5272	0.3	69	77.0393	3.1	123	146.0101	0.5
17	37.9896	0.4	70	78.0475	1.3	124	147.0055	2.3
18	38.0306	0.4	71	79.0198	0.4	125	148.0141	0.3
19	39.0375	1.1	72	79.0536	0.5	126	149.0259	0.6
20	39.9765	3.7	73	81.0200	0.4	127	149.0579	0.2
21	41.0538	0.7	74	81.0718	0.7	128	150.0325	1.9
22	42.0256	0.3	75	82.0727	0.2	129	150.9051	5.6
23	43.0328	1.7	76	83.0534	0.2	130	151.0437	0.2
24	43.0686	0.8	77	83.0887	0.4	131	151.1570	0.3
25	44.0039	2.3	78	84.0564	0.2	132	151.9014	0.3
26	45.0471	0.9	79	85.0325	0.4	133	151.9151	0.3
27	50.0229	1.2	80	87.0478	0.6	134	153.0114	0.2
28	51.0143	0.2	81	89.0421	0.7	135	153.0315	0.4
29	51.0288	0.8	82	91.0206	1.7	136	160.0403	0.3
30	51.5134	1.5	83	91.0564	1.0	137	161.0239	9.5
31	52.0146	0.4	84	92.0302	1.0	138	162.0322	8.7
32	52.0343	0.3	85	95.0156	1.7	139	163.0340	3.1
33	52.0389	0.4	86	95.0947	0.3	140	164.0341	0.4
34	53.0072	1.2	87	97.0716	0.2	141	165.0408	0.3
35	53.0448	0.3	88	97.0965	0.5	142	165.0619	0.3
36	53.0496	0.3	89	98.0756	0.6	143	168.9907	1.1
37	55.0240	0.5	90	101.0031	0.3	144	175.0007	1.3
38	55.0581	0.9	91	101.0117	0.2	145	177.0234	0.3
39	56.0703	0.2	92	101.0648	0.4	146	178.0245	1.3
40	57.0741	0.7	93	102.0127	0.4	147	179.0319	0.5
41	59.0151	5.1	94	102.0236	0.3	148	180.9864	0.3
42	59.0492	0.3	95	103.0218	9.2	149	190.0268	1.5
43	59.0542	0.4	96	104.0302	4.2	150	191.0361	4.0
44	60.0145	0.3	97	105.0360	1.7	151	192.0396	0.6
45	60.0200	0.4	98	106.0471	0.4	152	193.0515	8.9
46	62.0172	0.7	99	107.0165	0.3	153	194.0541	1.2
47	63.0249	2.1	100	107.0513	1.0	154	195.0613	0.3
48	63.4536	0.7	101	109.1041	0.3	155	204.9922	0.4
49	64.0303	0.4	102	110.0134	0.2	156	205.0338	0.2
50	65.0364	0.5	103	111.0239	0.7	157	207.0240	1.2
51	65.0439	0.6	104	117.0350	0.3	158	208.0358	0.4
52	65.5073	1.4	105	118.0021	0.6	159	219.0192	0.3
53	66.0093	0.5	106	119.0143	7.3	160	219.0417	0.2

NUMBER 255

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

EPA-287 (Cin.)
(4-76)

BEGIN FIRST LINE OF TEXT HERE

TYPING GUIDE SHEET

CENTER OF PAGE

TOP OF IMAGE AREA

DROPPED HEAD; BEGIN SECTIONS HERE

PEAK NO.	MASS	%HT. MOD.
161	220.0231	0.4
162	220.9726	0.3
163	221.0437	100.0
164	221.1562	0.3
165	221.1936	0.2
166	222.0489	24.0
167	223.0503	3.9
168	224.0496	0.6
169	235.0630	0.3
170	244.9681	0.4
171	248.0052	0.6
172	250.0169	0.4
173	251.0598	0.8
174	252.0647	7.3
175	253.0572	1.3
176	253.8092	3.5
177	265.8132	1.6
179	278.8128	1.0
181	405.7059	0.6

6-1/2"

9-1/8"

NUMBER 255

BEGIN LAST LINE OF TEXT

BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS

3/8"

PAGE NUMBER

EPA-287 (Cin.)
(4-76)

PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.
1	24.0282	1.5	54	84.0615	1.7	108	193.0490	2.2
2	27.0497	3.5	55	85.0657	1.5	109	193.9431	2.0
3	28.0305	682.5	56	86.9654	4.8	110	198.9027	2.0
4	29.0270	11.0	57	87.0481	2.7	111	209.9036	1.2
5	29.0635	4.0	58	88.0587	1.2	112	214.9794	1.8
6	30.0356	1.5	59	91.0582	2.3	113	221.0439	100.0
7	31.0402	4.0	60	95.0229	2.8	114	222.0495	14.3
8	32.0107	286.7	61	95.0914	2.8	115	222.9381	1.8
9	32.0487	2.3	62	95.9819	2.5	116	223.0457	2.5
10	34.0121	1.2	63	96.0580	1.7	117	224.9552	1.5
11	34.9863	1.8	64	96.9940	2.0	118	226.9093	15.0
12	35.9938	10.7	65	97.1019	1.5	119	227.9093	2.2
13	37.9899	3.2	66	99.9967	1.2	120	228.9042	16.2
14	39.0382	3.8	67	103.0060	1.7	121	230.9005	5.7
15	39.9768	29.2	68	103.0223	3.2	122	234.9827	2.0
16	41.0541	5.5	69	103.0495	1.7	123	240.9254	1.7
17	42.0504	3.0	70	104.0304	5.7	124	242.9200	2.0
18	43.0330	10.7	71	105.0318	2.5	125	253.8882	23.8
19	43.0698	7.0	72	109.1090	1.8	126	258.9334	14.5
20	44.0050	12.2	73	111.0473	3.3	127	259.9524	2.3
21	45.0464	8.5	74	115.0763	2.5	128	260.9374	13.2
22	47.0051	1.5	75	116.9960	3.5	129	261.9351	1.8
23	48.9949	1.5	76	119.0254	2.2	130	261.9562	1.7
24	51.0305	2.5	77	120.0219	4.2	131	262.9404	5.7
25	53.0095	3.7	79	127.9135	9.8	132	264.9710	2.8
26	55.0250	3.5	80	130.0714	1.8	133	265.8063	9.5
27	55.0597	6.8	81	131.0020	1.7	135	278.8076	6.5
28	56.0651	2.7	82	135.0457	1.5	136	279.0467	1.8
29	57.0328	1.7	83	139.9071	8.7	137	291.9986	1.8
30	57.0743	6.2	84	141.9312	3.5	139	405.7112	5.5
31	58.0479	1.5	85	146.9942	3.3			
32	59.0161	14.3	86	149.0561	4.2			
33	59.0513	2.5	87	150.0240	1.5			
34	63.0292	1.8	88	150.0424	2.2			
35	63.4542	5.3	89	150.9041	36.3			
36	67.0550	3.7	90	151.9085	2.0			
37	68.9958	13.2	91	156.9722	3.8			
38	69.0716	6.0	92	158.9189	8.5			
39	70.0773	2.0	93	160.9177	10.0			
40	71.0874	3.2	94	161.0164	2.5			
41	72.9961	2.8	95	161.0392	2.3			
42	73.0642	3.2	96	162.0348	2.5			
43	74.0152	3.7	97	162.9127	4.2			
44	74.0384	3.7	98	163.0426	2.8			
45	75.0256	7.5	99	168.9920	8.2			
46	75.0484	2.8	100	174.9359	1.8			
47	76.0337	3.7	101	174.9937	3.0			
48	77.0394	2.8	102	189.9769	1.8			
49	79.0549	2.3	103	190.9307	3.2			
50	81.0706	2.5	104	191.0326	4.7			
51	82.0406	1.5	105	191.9414	2.0			
52	82.0777	1.8	106	192.0487	1.3			
53	83.0922	4.8	107	192.9304	2.7			

NUMBER 258

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA: OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

DPA-187 (Cin.)
(4-76)

PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.
1	24.0257	1.9	54	82.0773	2.8
2	24.0276	4.1	55	83.0575	1.5
3	27.0478	3.4	56	83.0878	3.4
4	28.0300	882.5	57	85.0314	2.4
5	29.0265	14.2	58	85.0667	2.8
6	29.0625	6.0	59	87.0511	3.9
7	31.0398	4.5	60	95.0178	7.5
8	32.0111	381.7	61	95.0887	3.2
9	35.9940	9.7	62	96.9911	2.4
10	37.9913	2.2	63	97.1124	2.2
11	39.0378	6.2	64	98.0779	2.6
12	39.9761	35.1	65	102.0152	3.0
13	41.0537	9.9	66	103.0359	4.1
14	42.0259	2.8	67	105.0314	2.2
15	42.0481	2.2	68	108.0008	2.4
16	42.0643	2.4	69	115.0407	3.0
17	43.0323	12.1	70	119.0019	4.3
18	43.0403	3.7	71	120.0264	2.4
19	43.0683	10.6	73	127.9147	9.5
20	44.0043	14.2	74	130.9938	2.8
21	45.0123	1.9	75	133.0313	5.8
22	45.9475	7.5	76	134.0349	6.9
23	50.0011	2.6	77	138.9039	11.9
24	51.0271	1.7	78	141.9279	1.9
25	51.0317	2.8	79	141.9420	2.8
26	51.5122	2.2	80	141.9598	2.2
27	53.0077	2.6	81	143.0301	3.4
28	53.0369	1.9	82	143.0450	3.0
29	55.0215	4.5	83	147.9942	11.9
30	55.0590	8.0	84	148.0139	1.7
31	56.0637	3.7	85	150.9047	54.3
32	57.0378	2.6	86	151.9097	2.6
33	57.0737	6.2	87	153.0365	2.6
34	58.0469	2.8	88	161.0233	10.3
35	59.0157	19.8	89	162.0326	4.5
36	59.0544	2.8	90	163.0403	3.2
37	63.0240	4.1	91	168.9837	11.0
38	63.4542	6.2	92	174.9764	3.2
39	67.0537	4.1	93	176.9820	2.4
40	68.9957	15.7	94	193.0478	20.9
41	69.0338	1.9	95	194.0554	2.8
42	69.0707	5.2	96	194.0778	1.9
43	71.0493	2.9	97	207.0274	5.0
44	71.0361	2.4	98	221.0446	100.0
45	71.0879	4.7	99	222.0470	13.8
46	71.0958	2.4	100	223.0494	3.0
47	73.0568	4.5	101	252.0644	20.7
48	74.0174	6.7	102	253.0659	2.2
49	74.0370	4.1	103	253.8104	20.2
50	75.0260	10.3	104	265.8034	11.4
51	75.0499	2.8	106	275.8121	9.3
52	76.0395	1.9	107	327.0915	3.0
53	77.0476	1.5	109	405.7229	7.1

NUMBER 265

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA: OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-78)

PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.
1	24.0260	10.4	54	75.0477	10.4	108	151.9129	4.5
2	27.0486	11.4	55	77.0389	9.4	109	152.9527	9.4
3	28.0309	*******	56	78.0448	6.9	110	153.0257	3.5
4	28.2565	5.0	57	81.0735	12.4	111	154.9413	6.9
5	29.0267	34.7	58	82.0793	11.9	112	154.9659	9.4
6	29.0629	21.8	59	83.0888	16.8	113	156.9513	4.5
7	31.0399	14.4	60	84.0609	9.9	114	156.9563	4.0
8	32.0110	844.1	61	85.0334	6.9	115	161.0256	4.5
9	32.0481	8.9	62	86.9670	6.4	116	167.0490	7.4
10	34.0133	4.5	63	86.9746	4.0	117	168.9888	21.3
11	34.9883	6.4	64	87.0492	20.3	118	175.0354	8.4
12	35.9940	33.2	65	89.0469	6.9	119	176.0491	29.2
13	37.9856	9.4	66	90.0488	6.4	120	183.9724	41.6
14	37.9906	9.9	67	91.0535	6.9	121	184.9751	6.4
15	39.0372	10.4	68	91.0620	7.9	122	185.9686	32.2
16	39.9762	75.7	69	95.0520	14.4	123	186.9677	5.4
17	41.0522	32.2	70	96.0351	4.5	124	186.9856	5.0
18	42.0621	9.4	71	97.0701	6.4	125	187.9721	9.4
19	43.0326	41.1	72	97.1035	13.4	126	193.0667	4.5
20	43.0690	29.7	73	98.0681	5.9	127	205.0513	5.0
21	44.0041	42.6	74	98.0772	8.4	128	207.0671	5.9
22	44.0377	4.5	75	101.0633	9.4	129	211.0755	8.4
23	45.0482	22.8	76	101.0715	4.5	130	218.9890	10.4
24	51.0287	6.4	77	103.0426	62.4	131	221.0417	6.3
25	51.0331	4.0	78	105.0411	5.9	132	234.0539	41.1
26	53.0439	7.4	79	108.9553	7.4	133	235.0633	73.8
27	54.0475	6.9	80	109.0065	11.9	134	236.0597	14.9
28	54.0522	7.9	81	109.0203	7.4	135	252.9205	4.5
29	54.0564	7.4	82	109.9327	5.4	136	253.8139	61.4
30	55.0219	13.4	83	110.9983	4.5	137	254.9272	5.9
31	55.0582	31.2	84	111.1171	5.4	138	255.0063	13.4
32	56.0659	13.9	85	113.0636	6.4	139	256.0145	3.5
33	57.0369	8.4	86	117.0349	5.4	140	256.9962	5.9
34	57.0725	25.7	87	118.0396	7.9	141	260.9462	7.4
35	59.0152	54.0	88	118.9912	11.4	142	260.9804	7.9
36	59.0417	4.5	89	120.9989	5.4	143	262.9641	5.9
37	59.0515	10.4	90	124.9527	9.4	144	265.8147	24.3
38	61.0310	8.9	92	126.9543	5.9	145	266.0827	7.4
39	62.0160	5.4	93	127.9135	28.2	147	278.8140	16.8
40	63.0249	6.4	94	133.0093	6.4	148	327.0766	5.4
41	63.4510	10.9	95	133.0463	10.9	149	334.9753	5.4
42	67.0528	18.3	96	138.9240	34.2	151	405.7185	14.9
43	68.0640	8.4	97	140.9670	3.5			
44	68.9955	45.0	98	141.9234	5.4			
45	69.0711	25.2	99	143.1083	5.9			
46	70.0764	8.4	100	146.9913	12.4			
47	71.0129	9.4	101	147.0453	5.0			
48	71.0242	4.5	102	148.0458	6.4			
49	71.0480	8.4	103	148.9694	5.4			
50	71.0864	11.4	104	149.0025	13.9			
51	72.9869	5.0	105	149.0603	6.4			
52	73.0637	8.4	106	150.9058	100.0			
53	74.0351	42.1	107	151.0016	5.4			

NUMBER 274

BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
BEGIN LAST LINE OF TEXT
3/8"
PAGE NUMBER

EPA-287 (Cin.)
(4-76)

PEAK NO.	MASS	%HT. MOD.
1	27.0485	3.3
2	28.0301	678.0
3	29.0264	11.8
4	29.0614	5.1
5	31.0378	3.5
6	31.0419	2.5
7	32.0104	283.3
8	35.3935	8.3
9	37.9684	2.2
10	39.0333	3.3
11	39.0383	2.8
12	39.9757	25.2
13	41.0527	8.1
14	43.0316	9.1
15	43.0636	6.6
16	44.0037	12.1
17	45.0472	14.2
18	49.9971	2.8
19	50.0197	3.1
20	51.0107	1.5
21	51.0221	1.8
22	55.0196	3.6
23	55.0572	7.5
24	56.0587	3.1
25	56.0665	3.1
26	57.0417	1.5
27	57.0724	10.3
28	59.0137	12.4
29	59.0503	2.2
30	63.0246	3.1
31	63.4542	4.6
32	67.0525	2.5
33	67.0585	2.5
34	68.0626	2.8
35	68.9962	11.1
36	69.0342	2.5
37	69.0702	5.8
38	70.0423	1.5
39	71.0509	3.8
40	71.0871	4.3
41	73.0597	2.8
42	73.0713	1.8
43	74.0170	5.0
44	74.0382	4.1
45	75.0237	7.5
46	76.0298	7.8
47	77.0373	3.8
48	78.0489	1.7
49	79.0520	1.5
50	81.0726	4.1
51	82.0927	2.2
52	83.0864	4.1
53	84.0556	1.3
54	84.0906	1.8
55	85.1003	2.5
56	87.0465	3.8
57	89.0337	1.5
58	91.0558	2.2
59	95.0932	2.8
60	96.0951	3.1
61	97.1067	3.8
62	103.0069	2.3
63	103.0256	3.1
64	103.0480	1.8
65	104.0264	10.9
66	105.0347	1.7
67	108.0001	2.2
68	109.1047	2.2
69	109.1126	1.7
70	117.0581	1.2
71	119.0017	6.0
72	120.0236	3.6
73	121.0100	1.7
74	121.1038	1.5
75	125.1007	1.7
77	127.0412	1.7
78	127.9124	11.4
79	132.0203	3.0
80	135.0208	1.5
81	138.9024	7.8
82	141.9249	3.0
83	141.9366	1.8
84	141.9626	1.5
85	146.9943	2.6
86	148.0113	2.0
87	149.0592	5.5
88	150.0318	2.5
89	150.9048	37.6
90	153.0352	2.5
91	161.0121	1.5
92	162.0368	2.0
93	163.0446	4.1
94	168.9902	8.4
95	180.9848	1.8
96	189.0455	1.3
97	191.0196	1.7
98	191.0433	2.3
99	193.0530	1.5
100	205.0347	2.3
101	205.0592	1.3
102	221.0466	100.0
103	222.0507	16.9
104	223.0515	3.5
105	231.0253	1.7
106	246.0403	3.5
107	248.0756	1.8
108	253.8084	22.5
109	263.0581	4.8
110	265.8110	9.8
112	278.8158	7.9
113	281.0659	1.5
114	284.9775	1.8
115	327.0678	1.7
116	334.9583	1.8
117	335.0162	1.5
119	405.7139	3.5

NUMBER 304

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"
PAGE NUMBER

EPA-287 (Cin.)
(4-76)

PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.
1	27.0467	1.3	54	78.0423	0.6	108	162.0301	5.2
2	28.0297	194.5	55	79.0533	0.7	109	163.0371	1.2
3	29.0251	2.9	56	81.0703	1.7	110	168.9888	2.2
4	29.0607	1.5	57	82.0764	0.9	111	174.9938	0.3
5	31.0402	1.1	58	83.0465	0.6	112	175.0260	0.4
6	32.0099	75.0	59	83.0876	1.8	113	177.0198	3.4
7	32.0425	0.5	60	84.0582	1.4	114	178.0266	0.6
8	34.0117	0.4	61	85.0312	0.8	115	180.9939	0.5
9	35.9924	2.3	62	85.1028	1.0	116	183.0769	0.4
10	37.9975	1.3	63	85.1107	0.7	117	185.1202	0.5
11	39.0358	1.3	64	87.0456	1.1	118	190.0250	6.9
12	39.9751	8.4	65	88.0539	0.7	119	191.0374	0.9
13	41.0525	3.2	66	91.0189	0.6	120	193.0344	0.6
14	42.0583	0.5	67	91.0593	0.9	121	205.0129	1.0
15	43.0306	2.7	68	93.0733	0.8	122	207.0282	0.7
16	43.0671	2.9	69	95.0856	2.0	123	207.0678	0.6
17	44.0018	3.8	70	95.0946	0.7	124	208.0458	0.4
18	45.0443	2.2	71	96.0917	0.7	125	219.0120	0.7
19	49.9974	0.6	72	96.1007	0.4	126	220.0305	1.2
20	50.0214	1.2	73	97.0695	1.2	127	220.0661	0.9
21	51.0251	0.5	74	97.1065	1.1	128	221.0496	1.8
22	53.0076	0.8	75	98.0791	0.7	129	222.0338	0.5
23	53.0427	1.0	76	101.0019	0.7	130	222.0563	0.4
24	54.0476	0.5	77	102.0113	0.7	131	223.0581	0.8
25	55.0201	1.3	78	103.0238	1.3	132	233.0105	2.8
26	55.0572	2.8	79	104.0278	2.5	133	235.0479	0.8
27	56.0651	1.1	80	105.0343	0.9	134	236.0467	0.5
28	57.0721	2.2	81	105.0674	0.5	135	240.9875	0.4
29	58.0470	0.9	82	109.1085	0.7	136	243.0345	1.6
30	59.0140	5.0	83	111.1211	0.6	137	249.0410	1.5
31	59.0510	0.7	84	113.0255	0.3	138	251.0570	2.9
32	60.0192	0.3	85	118.0118	0.7	139	252.0403	0.5
33	62.0157	1.2	86	119.0034	1.1	140	252.0648	0.8
34	63.0198	0.8	87	120.0122	0.7	141	253.8087	6.5
35	63.0250	1.1	88	121.0306	0.4	142	255.0058	0.6
36	63.4508	1.9	89	123.1218	0.6	143	255.0635	0.4
37	65.0364	0.9	90	124.0159	2.7	144	263.0597	0.6
38	67.0535	1.0	91	125.1275	0.4	145	265.0159	0.6
39	68.0554	0.6	93	127.9114	3.0	146	265.8143	2.6
40	68.0615	0.7	94	131.0018	0.5	148	278.8150	1.9
41	68.9958	2.9	95	132.0233	0.6	149	279.0501	100.0
42	69.0355	0.3	96	133.0273	0.9	150	280.0552	14.8
43	69.0593	1.9	97	134.0346	1.3	151	281.0591	3.0
44	70.0679	0.8	98	137.1321	0.5	152	284.9824	0.3
45	71.0503	1.4	99	138.9051	2.2	153	285.0071	0.3
46	71.0854	1.3	100	141.9303	0.5	154	286.9586	0.5
47	73.0051	0.5	101	143.0864	0.3	155	290.9938	0.7
48	73.0580	0.5	102	146.9991	2.3	156	310.0717	3.1
49	73.0672	0.6	103	148.0160	0.5	157	311.0674	1.0
50	74.0255	2.2	104	149.0247	0.7	158	318.9930	1.0
51	75.0243	3.4	105	150.9033	10.1	159	320.9835	0.6
52	76.0304	2.3	106	151.9073	0.7	160	329.0610	1.0
53	77.0390	1.4	107	161.0237	5.0	161	334.9840	0.4
						162	350.0095	0.4
						164	485.7090	1.0

NUMBER 321

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"
PAGE NUMBER
EPA-287 (Cin.)
(4-76)

PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.
1	27.0481	0.5	54	75.0441	0.5	108	133.0293	1.9
2	28.0295	145.9	55	76.0305	0.9	109	134.0363	1.7
3	28.0555	0.7	56	77.0021	0.4	110	135.0268	0.5
4	29.0266	2.8	57	77.0411	0.7	111	135.0473	0.7
5	29.0622	1.3	58	78.0475	0.8	112	138.9038	1.2
6	31.0394	0.3	59	79.0552	0.6	113	140.0138	0.6
7	32.0181	56.6	60	81.0738	0.9	114	140.0330	0.7
8	32.0475	0.5	61	82.0781	0.7	115	141.9225	0.3
9	34.0131	0.4	62	83.0876	1.1	116	145.9903	0.4
10	34.9848	0.3	63	84.0564	0.5	117	147.0032	1.4
11	35.9935	2.3	64	84.0655	0.8	118	148.0146	0.4
12	37.9879	0.5	65	84.0965	0.4	119	149.0190	0.7
13	39.0375	0.9	66	85.0325	0.4	120	150.0252	0.5
14	39.9767	5.2	67	85.0692	0.5	121	150.9068	8.2
15	41.0515	2.0	68	85.0991	0.4	122	153.0162	0.2
16	42.0233	0.4	69	86.0193	0.5	123	153.0305	0.5
17	43.0321	2.2	70	87.0494	1.1	124	160.0137	0.5
18	43.0601	1.9	71	90.0144	0.5	125	161.0251	3.0
19	44.0032	2.7	72	91.0277	0.4	126	162.0314	5.3
20	45.0476	5.5	73	91.0533	0.5	127	163.0326	1.0
21	50.0232	0.6	74	93.0384	0.5	128	164.0411	0.5
22	51.0277	0.7	75	93.0709	0.4	129	165.0140	0.7
23	53.0024	0.9	76	94.0860	0.3	130	165.0403	0.6
24	53.0086	0.6	77	95.0887	0.7	131	168.9918	1.9
25	53.0426	0.6	78	96.0958	0.5	132	175.0136	0.4
26	54.0477	0.4	79	97.1063	0.7	133	177.0174	1.8
27	55.0215	0.9	80	98.0769	1.0	134	178.0287	1.6
28	55.0597	2.1	81	99.0527	0.3	135	183.0465	0.2
29	56.0663	1.1	82	99.0913	0.4	136	190.0284	1.5
30	57.0380	0.6	83	101.0029	0.6	137	191.0409	0.9
31	57.0720	1.7	84	101.0239	0.3	138	193.0569	0.7
32	57.0819	1.1	85	102.0141	1.2	139	194.0518	0.6
33	58.0431	0.4	86	103.0236	2.3	140	201.0244	0.6
34	59.0148	4.0	87	104.0279	1.0	141	203.0487	0.5
35	59.0500	0.6	88	105.0410	1.9	142	205.0153	1.7
36	62.0171	0.9	89	105.0693	0.3	143	206.0133	0.4
37	63.0242	1.1	90	108.0976	0.3	144	207.0629	1.8
38	63.4504	1.0	91	109.0717	0.4	145	208.0436	0.8
39	63.4579	0.5	92	109.1027	0.7	146	219.0307	2.1
40	65.0417	0.4	93	110.1120	0.5	147	220.0368	2.9
41	65.5073	0.9	94	111.0816	0.5	148	221.0432	2.2
42	67.0530	0.9	95	114.0714	0.3	149	222.0455	0.5
43	68.0605	0.6	96	118.0090	0.6	150	223.0710	0.4
44	68.9942	2.2	97	119.0057	0.7	151	231.0370	0.7
45	69.0333	0.7	98	119.0602	0.2	152	233.0132	2.4
46	69.0701	2.2	99	121.0300	0.4	153	233.9794	0.3
47	70.0691	0.5	100	121.1068	0.4	154	234.0133	0.4
48	71.0481	0.6	101	124.0106	1.3	155	247.0284	0.3
49	71.0856	1.0	103	127.9150	2.0	156	248.0351	0.8
50	73.0019	0.5	104	129.0568	0.6	157	249.0364	1.4
51	73.0663	1.0	105	130.9911	0.6	158	251.0578	1.8
52	74.0231	2.5	106	131.0058	0.5	159	252.0260	0.3
53	75.0227	3.1	107	132.0254	0.4	160	253.8083	4.6

NUMBER 330

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

EPA-287 (Cin.)
(4-76)

PEAK NO.	MASS	%HT. MOD.
161	255.0263	0.5
162	256.0181	0.2
163	261.0411	2.4
164	262.0478	1.0
165	263.0455	0.3
166	265.0313	1.1
167	265.0107	2.2
168	277.0287	0.3
169	277.0612	0.3
171	278.0168	1.2
172	279.0534	100.0
173	280.0564	14.6
174	281.0566	2.7
175	282.0611	0.4
176	287.0323	0.3
177	292.0578	1.5
178	293.0503	0.4
179	293.0784	0.5
180	301.0690	1.1
181	310.0812	0.4
182	329.0679	1.9
183	330.0695	0.5
184	360.0840	0.9
185	405.7124	1.0

Number 330

6-1/2"
9-1/8"
BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.
1	27.8472	4.7	54	79.0542	4.2	107	126.0383	2.8
2	27.0499	4.0	55	81.0720	5.6	108	126.0491	2.7
3	28.0290	680.2	56	82.0926	2.8	110	127.0393	2.5
4	29.0260	11.8	57	83.0884	8.0	111	127.0574	3.2
5	29.0611	7.3	58	84.0591	3.5	112	127.9131	11.8
6	30.0300	1.7	59	84.0939	1.5	113	128.0241	1.8
7	31.0386	3.8	60	85.0336	2.5	114	129.0491	1.8
8	31.0439	2.0	61	85.1040	2.8	115	130.9934	1.5
9	32.0098	283.7	62	86.0100	1.8	116	132.0149	2.3
10	32.0444	3.0	63	86.0193	2.5	117	133.0279	3.5
11	32.0477	3.2	64	86.9646	1.5	118	133.0394	1.5
12	34.0137	2.2	65	87.0209	2.5	119	133.0604	1.3
13	35.9928	12.0	66	87.0443	4.5	120	134.0409	2.3
14	37.9897	3.2	67	89.0409	2.8	121	137.9870	1.5
15	39.0376	4.7	68	90.0145	1.7	122	138.0331	1.7
16	39.9757	25.1	69	91.0578	4.5	123	138.9058	7.1
17	41.0520	9.6	70	93.0731	2.5	124	139.0393	1.2
18	42.0600	3.2	71	94.0841	2.2	125	139.0686	1.2
19	43.0318	11.0	72	95.0917	5.3	126	139.0815	1.3
20	43.0682	9.8	73	96.0603	2.5	127	141.9243	2.5
21	44.0028	16.1	74	96.1005	1.8	128	146.9961	5.5
22	45.0458	11.1	75	97.0599	1.7	129	149.0234	5.3
23	49.9994	2.3	76	97.0691	2.8	130	150.0359	1.8
24	53.0050	3.2	77	97.1056	3.5	131	150.9027	33.4
25	53.0441	3.3	78	98.0742	3.7	132	151.9080	1.7
26	54.0525	3.3	79	98.0834	1.7	133	153.0354	1.8
27	55.0218	4.7	80	99.9248	1.5	134	161.0257	4.5
28	55.0576	14.1	81	99.9405	2.5	135	162.0332	8.6
29	56.0641	3.5	82	102.0124	2.0	136	163.0283	3.7
30	57.0375	2.8	83	103.0209	3.8	137	163.0589	1.5
31	57.0731	8.3	84	103.0435	3.2	138	164.0362	1.7
32	59.0137	16.9	85	104.0288	8.0	139	168.9882	9.6
33	59.0513	6.3	86	105.0337	3.3	140	177.0141	2.5
34	61.0249	1.8	87	107.0876	2.3	141	177.9925	1.8
35	63.0236	4.0	88	108.0976	2.3	142	178.0419	1.2
36	63.4548	3.2	89	108.9817	1.7	143	184.0385	1.5
37	65.0425	2.0	90	109.1037	3.2	144	190.0254	3.3
38	67.0538	6.3	91	111.0812	2.5	145	191.0076	1.5
39	68.0607	3.5	92	111.1134	2.2	146	191.0386	1.5
40	68.9952	11.5	93	111.1243	2.0	147	193.0500	1.8
41	69.0328	2.0	94	112.0910	1.2	148	197.0316	1.7
42	69.0692	10.6	95	113.0318	1.5	149	202.0292	1.8
43	70.0774	2.7	96	114.0476	2.2	150	205.0236	1.3
44	71.0504	4.0	97	114.0708	1.5	151	207.0623	3.5
45	71.0845	4.8	98	115.0532	2.7	152	211.0453	2.5
46	73.0652	5.5	99	119.0011	3.5	153	212.0448	2.8
47	74.0167	3.5	100	120.0215	1.5	154	213.0112	1.8
48	74.0364	4.0	101	121.1085	1.8	155	218.0255	1.5
49	75.0225	5.5	102	123.1179	1.8	156	219.0217	1.7
50	75.0452	2.5	103	124.0154	3.8	157	220.9344	1.7
51	76.0301	4.8	104	124.1202	1.8	158	221.0401	4.2
52	77.0377	4.5	105	125.0392	2.3	159	224.9954	2.2
53	78.0477	3.7	106	125.0525	1.5	160	227.0264	2.5

NUMBER 355

TYPING GUIDE SHEET
BEGIN FIRST LINE OF TEXT HERE
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD; BEGIN SECTIONS HERE
BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"
PAGE NUMBER
EPA-287 (Cin.)
(4-76)

PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.
161	231.0243	3.0	215	299.0341	4.0
162	231.0465	1.8	216	300.9461	2.3
163	232.0437	2.2	217	301.0671	15.8
164	233.0118	4.3	218	302.0502	5.1
165	233.0486	1.3	219	303.0340	2.0
166	234.0464	1.5	220	307.0455	3.8
167	249.0390	3.5	221	311.0423	1.5
168	251.0561	1.8	222	314.0411	3.7
169	253.8049	17.3	223	315.0072	2.5
170	255.0222	8.6	224	315.9925	1.5
171	256.0433	1.7	225	319.0504	3.2
172	259.0355	1.3	226	320.0706	2.2
173	261.0372	7.1	227	321.0437	1.5
174	262.0329	2.7	228	325.9997	2.8
175	263.0264	1.8	229	326.0369	3.0
176	263.0578	2.2	230	327.0477	2.2
177	264.0140	2.0	231	329.0675	31.1
178	264.0676	3.2	232	330.0681	8.3
179	264.9655	2.8	233	330.9988	6.5
180	265.0027	3.0	234	332.0040	1.8
181	265.0520	1.7	235	332.9715	3.5
182	265.0932	1.8	236	335.0663	15.3
183	265.8064	11.6	237	336.0664	4.5
184	267.0040	1.5	238	336.1111	2.0
185	269.0331	2.0	239	337.0611	1.8
186	270.0152	1.8	240	339.0201	3.2
187	270.0504	3.0	241	344.0977	1.5
188	270.0713	2.2	242	355.0752	1.3
189	271.0372	1.5	243	360.0857	11.8
190	271.0622	2.5	244	361.0979	2.8
191	273.0659	1.8	245	362.0804	1.8
192	276.0552	2.0	246	404.0130	1.8
194	278.0307	1.5	248	405.7121	3.8
195	278.8112	4.0			
196	279.0492	100.0			
197	280.0536	15.3			
198	281.0395	4.3			
199	282.0483	2.0			
200	283.0219	8.5			
201	284.9837	3.0			
202	286.0369	2.8			
203	289.0104	1.7			
204	289.0474	3.5			
205	290.0342	3.8			
206	291.0061	1.8			
207	291.0413	1.8			
208	293.0383	3.8			
209	295.0000	2.2			
210	295.0344	1.7			
211	295.9834	1.5			
212	296.0342	1.2			
213	296.9974	1.7			
214	298.9492	3.7			

9-1

NUMBER 355

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

EPA-287 (Cin.)
(4-76)

PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.
1	27.0474	8.7	54	74.0370	12.7	107	123.1158	7.0
2	28.0294******		55	75.0244	15.1	108	125.0282	3.0
3	28.0432	4.3	56	75.0411	4.7	109	125.1008	4.3
4	28.0547	3.3	57	76.0321	7.0	111	127.0691	4.7
5	29.0254	25.4	58	77.0399	6.0	112	127.9160	24.7
6	29.0615	15.4	59	78.0482	6.4	113	129.0649	4.3
7	31.0394	7.0	60	79.0537	7.0	114	130.0383	2.3
8	32.0059	555.9	61	81.0730	14.4	115	130.0641	2.7
9	32.0458	7.4	62	82.0796	11.0	116	130.9894	5.0
10	32.0499	3.3	63	83.0876	18.4	117	132.0202	5.0
11	35.9935	23.1	64	84.0566	6.4	118	133.0324	6.4
12	37.9897	11.7	65	84.0925	6.4	119	133.0989	2.7
13	39.0383	8.7	66	85.0321	6.4	120	134.0403	5.4
14	39.9758	52.2	67	85.0630	5.4	121	135.1071	3.3
15	41.0522	21.1	68	85.0714	4.7	122	135.1228	2.7
16	42.0597	6.4	69	85.1023	4.3	123	137.0457	4.3
17	43.0320	22.4	70	85.1124	4.0	124	137.0971	4.0
18	43.0686	26.4	71	86.0149	3.7	125	137.1345	2.3
19	44.0034	29.1	72	86.9652	3.7	126	138.9043	18.4
20	45.0471	19.4	73	87.0471	8.0	127	139.0182	3.7
21	49.9985	8.7	74	89.0378	3.7	128	139.0497	3.3
22	50.0033	4.0	75	91.0588	5.4	129	141.0607	4.0
23	50.0231	2.7	76	93.0738	7.0	130	141.9268	5.0
24	51.0249	5.4	77	93.0840	4.0	131	146.9947	10.4
25	51.0305	7.0	78	94.0793	3.7	132	149.0243	49.5
26	51.9932	3.7	79	95.0538	4.0	133	150.0321	8.7
27	53.0084	6.0	80	95.0836	12.7	134	150.9044	71.9
28	53.0438	5.0	81	96.0991	6.7	135	151.0475	4.0
29	54.0515	5.7	82	97.0278	3.0	136	151.0713	3.7
30	55.0215	8.0	83	97.0559	5.0	137	151.9125	3.7
31	55.0572	22.4	84	97.1012	8.7	138	153.0225	5.0
32	56.0641	11.7	85	97.1153	3.0	139	161.0276	8.4
33	57.0382	6.4	86	98.0772	8.4	140	162.0322	11.7
34	57.0721	39.8	87	101.0004	3.0	141	163.0387	5.0
35	58.0438	5.7	88	101.0594	6.7	142	164.9932	2.3
36	59.0152	41.1	89	103.0225	7.0	143	165.0246	3.0
37	59.0515	6.7	90	104.0250	6.4	144	167.0354	19.4
38	62.0113	3.7	91	105.0344	4.3	145	168.9693	18.4
39	62.0174	4.3	92	109.0284	2.7	146	177.0547	4.0
40	63.0243	6.4	93	109.1042	7.0	147	178.0239	3.7
41	63.4516	5.0	94	110.1082	3.3	148	178.0500	3.3
42	65.0377	5.4	95	111.1236	8.0	149	180.9883	4.0
43	67.0542	11.0	96	112.1207	4.7	150	190.0266	6.4
44	68.0644	10.0	97	112.1333	6.4	151	191.1793	5.0
45	68.9942	22.7	98	113.0323	3.0	152	199.0377	3.0
46	69.0365	6.0	99	113.0424	2.3	153	201.0178	3.0
47	69.0681	23.7	100	113.1361	8.7	154	205.0359	4.7
48	70.0767	14.7	101	115.0383	5.0	155	206.0592	3.3
49	71.0487	6.4	102	118.0434	4.3	156	206.0779	2.7
50	71.0840	26.1	103	118.9976	8.7	157	207.0294	5.4
51	73.0246	3.7	104	121.1062	7.0	158	207.0516	7.4
52	73.0669	10.4	105	123.0194	2.7	159	211.0339	3.7
53	74.0161	11.7	106	123.0509	3.0	160	213.0242	3.3

NUMBER 370

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.
161	213.0523	2.7	215	302.0735	6.7
162	218.0179	4.3	216	302.9779	3.7
163	218.0414	3.3	217	307.0414	6.4
164	219.0138	4.7	218	309.0567	5.4
165	219.0315	5.0	219	311.0486	5.7
166	220.0392	6.0	220	312.0468	3.7
167	221.0463	9.0	221	315.0482	4.3
168	225.0194	3.0	222	315.9960	3.0
169	229.0564	3.0	223	319.0463	10.0
170	233.0187	4.0	224	320.0700	5.0
171	234.9857	3.0	225	321.0021	3.3
172	235.0546	5.4	226	321.0564	3.7
173	245.0169	3.3	227	327.0670	5.4
174	245.0412	3.7	228	328.9576	4.7
175	249.0402	6.4	229	329.0557	14.4
176	252.0514	3.7	230	330.0595	4.3
177	253.8095	40.8	231	330.9639	5.0
178	255.0344	5.4	232	332.9620	5.0
179	256.0229	2.3	233	333.0842	4.3
180	261.0406	11.0	234	335.0119	5.0
181	262.0373	4.7	235	337.0530	12.7
182	263.0307	3.0	236	342.0861	3.7
183	263.0565	5.0	237	343.0688	3.7
184	263.0794	3.0	238	344.0569	3.7
185	264.0435	3.3	239	347.0556	4.7
186	264.0750	3.3	240	349.0549	4.7
187	265.0015	4.3	241	359.9833	3.7
188	265.8090	17.1	242	360.0626	8.0
189	267.0072	4.0	243	374.0781	4.3
190	271.0537	3.7	245	405.7049	11.0
191	276.0233	6.4			
192	277.0266	10.4			
193	277.0770	4.3			
195	278.0530	3.0			
196	278.8130	13.0			
197	279.0534	100.0			
198	279.1618	6.4			
199	280.0570	18.1			
200	281.0523	5.4			
201	283.0317	8.7			
202	284.9831	3.7			
203	286.0383	6.7			
204	287.0560	4.7			
205	287.1032	3.7			
206	289.0379	7.7			
207	291.0566	4.3			
208	293.0492	23.1			
209	294.0578	3.7			
210	295.0459	3.3			
211	297.0332	3.3			
212	298.9898	4.0			
213	299.0343	6.0			
214	301.0689	11.7			

NUMBER 370

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.
1	27.0467	4.4	54	74.0303	8.6	107	109.1043	5.4
2	27.0527	1.6	55	75.0226	6.7	108	110.1100	2.8
3	28.0283	595.2	56	75.0450	4.4	109	111.0820	3.5
4	28.0522	2.2	57	76.0288	3.6	110	111.1170	2.2
5	29.0248	12.4	58	77.0011	1.5	111	112.0915	2.5
6	29.0613	6.4	59	77.0094	2.3	112	113.0372	1.7
7	31.0389	4.9	60	77.0370	4.4	113	114.0480	1.2
8	32.0095	235.9	61	78.0458	2.5	114	115.0422	2.0
9	32.0450	2.5	62	79.0543	4.5	115	115.0633	2.3
10	35.9924	11.9	63	81.0713	6.8	116	118.0000	1.5
11	37.9869	4.8	64	82.0770	4.2	117	118.0136	1.6
12	39.0354	3.6	65	83.0476	2.3	118	118.0546	1.7
13	39.9744	23.0	66	83.0852	8.1	119	118.9948	2.5
14	40.0444	1.3	67	84.0594	3.1	120	119.0804	2.2
15	41.0515	14.1	68	84.0919	1.7	121	121.1045	2.8
16	42.0602	2.2	69	85.0279	1.6	122	123.0776	3.1
17	43.0223	1.5	70	85.0672	1.7	123	123.1192	3.1
18	43.0312	12.6	71	85.1047	4.1	124	125.0323	1.3
19	43.0670	12.1	72	86.0095	2.6	125	125.0975	2.0
20	44.0022	19.0	73	87.0238	2.3	126	125.1324	1.6
21	45.0455	11.6	74	87.0317	1.7	127	126.0657	1.9
22	49.9988	4.7	75	87.0466	6.0	129	127.0353	2.2
23	50.0210	2.0	76	88.0556	2.5	130	127.0490	2.0
24	51.0281	2.3	77	89.0139	1.2	131	127.9119	10.0
25	51.9941	1.6	78	89.0387	2.0	132	129.0384	1.0
26	53.0061	2.3	79	89.0485	1.9	133	129.0683	1.6
27	53.0426	2.9	80	91.0458	1.3	134	132.0239	2.0
28	54.0487	3.1	81	91.0585	3.8	135	133.0217	2.2
29	55.0198	6.5	82	92.0654	1.6	136	133.0465	1.3
30	55.0564	14.0	83	93.0735	3.3	137	133.1022	2.2
31	56.0632	4.9	84	94.0683	1.9	138	135.1273	3.6
32	57.0348	3.5	85	94.0819	2.2	139	137.0371	1.5
33	57.0716	12.8	86	94.5104	1.9	140	138.9050	4.7
34	58.0428	2.3	87	94.5211	1.5	141	139.0424	1.5
35	59.0145	18.6	88	95.0521	1.5	142	139.0569	1.5
36	59.0515	3.3	89	95.0887	6.5	143	141.0670	2.5
37	61.0294	1.6	90	96.0558	2.5	144	141.9230	2.5
38	63.0243	3.1	91	96.0972	4.1	145	143.0337	1.6
39	63.4473	1.3	92	97.0688	2.5	146	143.1145	1.6
40	65.0391	2.2	93	97.1048	6.8	147	146.0425	2.3
41	67.0531	8.9	94	98.0772	6.5	148	146.9889	3.3
42	68.0260	1.7	95	99.0395	2.3	149	147.0127	3.8
43	68.0594	4.5	96	99.0488	2.8	150	146.0088	2.2
44	68.9947	9.7	97	101.0477	1.3	151	149.0223	2.8
45	69.0332	2.6	98	101.0603	3.9	152	149.0594	1.5
46	69.0696	10.0	99	102.0157	3.1	153	149.1353	1.6
47	70.0752	4.8	100	103.0210	4.5	154	150.9051	21.5
48	71.0452	2.2	101	103.0521	1.3	155	151.9012	1.6
49	71.0531	3.2	102	104.0273	4.8	156	152.0549	2.0
50	71.0853	8.9	103	105.0338	2.2	157	153.0189	5.4
51	72.0439	1.2	104	105.0696	2.2	158	155.0407	1.0
52	73.0030	2.0	105	107.0926	2.6	159	161.0219	3.3
53	73.0642	4.5	106	108.0943	1.6	160	161.0684	1.5

NUMBER 408

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.	PEAK NO.	MASS	%HT. MOD.
161	161.1292	1.6	214	252.0401	1.6	268	312.0591	2.8
162	162.0299	10.6	215	253.0293	1.3	269	312.0759	2.3
163	163.0083	1.3	216	253.8015	12.6	270	313.0286	2.8
164	163.0408	5.8	217	261.0393	1.3	271	314.0176	1.6
165	163.1379	2.2	218	262.0329	2.2	272	315.0315	2.8
166	164.0365	1.2	219	263.0274	2.3	273	316.0750	1.3
167	167.0428	2.3	220	265.0473	2.6	274	317.0137	1.7
168	167.0650	1.3	221	265.8072	6.1	275	317.0590	1.6
169	168.9898	7.0	222	267.0648	1.5	276	319.0404	7.0
170	169.0509	1.9	223	268.0635	1.3	277	320.0118	1.9
171	171.0327	1.5	224	269.0453	2.2	278	320.0578	2.5
172	173.0167	2.2	225	271.0267	1.9	279	320.9908	1.0
173	175.0415	1.5	226	271.0721	1.5	280	321.0322	2.0
174	176.0493	1.7	227	273.0354	1.2	281	321.0650	2.0
175	177.0220	1.5	228	276.0553	1.7	282	322.0123	1.9
176	177.0466	2.5	229	277.0332	3.3	283	322.0500	1.2
177	178.0277	1.6	231	278.0212	1.3	284	323.0366	4.5
178	179.0395	1.3	232	278.8087	4.2	285	324.0555	1.9
179	179.0755	1.5	233	279.0498	4.5	286	325.0361	2.6
180	188.0276	1.6	234	280.0477	2.5	287	327.0618	2.0
181	190.0271	4.1	235	281.0140	1.9	288	327.1033	1.9
182	191.0334	1.9	236	281.0549	2.6	289	328.1042	1.5
183	191.1795	1.5	237	283.0096	2.6	290	329.0612	3.5
184	192.0509	2.0	238	283.0529	1.9	291	331.0539	1.9
185	195.0000	1.6	239	283.0828	1.0	292	332.0491	1.7
186	195.0176	1.9	240	285.0259	1.3	293	333.0291	2.5
187	202.0393	1.3	241	286.0355	1.6	294	333.0743	2.3
188	205.0235	2.0	242	287.0442	1.7	295	334.9746	2.9
189	206.0577	2.2	243	289.0332	3.9	296	335.0349	2.9
190	207.0354	3.3	244	290.0420	1.9	297	336.0506	1.6
191	207.0648	2.0	245	291.0236	5.2	298	337.0565	100.0
192	209.0563	2.5	246	292.0411	2.0	299	338.0621	17.6
193	216.0127	1.2	247	292.9944	1.6	300	339.0526	5.2
194	218.9890	1.2	248	293.0500	1.6	301	340.0337	1.5
195	219.0200	2.6	249	294.0691	1.2	302	342.0690	4.5
196	219.0483	2.8	250	295.0898	1.0	303	343.0747	3.2
197	220.0351	6.1	251	296.0650	2.5	304	343.1416	1.7
198	221.0439	5.7	252	297.0305	1.7	305	345.0038	1.9
199	230.9879	1.3	253	297.0722	1.9	306	345.0481	1.9
200	231.0121	2.2	254	299.0082	1.7	307	347.0184	3.3
201	232.9858	1.2	255	299.0564	2.2	308	347.0978	2.2
202	234.0484	2.0	256	301.0203	1.0	309	348.9825	1.3
203	235.0283	3.6	257	301.0666	1.5	310	349.0414	1.7
204	235.0662	1.5	258	302.0549	1.3	311	351.0174	1.6
205	237.0281	1.6	259	303.0618	1.3	312	351.0851	1.7
206	237.0558	1.3	260	304.0856	1.2	313	353.0204	4.8
207	245.0226	1.6	261	305.0357	1.9	314	354.0574	3.8
208	247.0351	1.6	262	307.0538	2.6	315	355.0570	4.9
209	247.0592	1.2	263	309.0587	2.3	316	355.9925	1.0
210	248.0248	2.5	264	310.0748	1.9	317	356.0580	2.0
211	249.0316	2.9	265	310.9833	1.3	318	356.9612	2.6
212	251.0132	2.0	266	311.0578	7.0	319	357.1054	1.3
213	251.0596	1.6	267	312.0203	2.3	320	359.0093	3.3

NUMBER 408

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

321	360.0513	2.0
322	363.0543	3.3
323	365.0329	1.6
324	369.0531	2.2
325	369.0850	2.2
326	373.0340	1.3
327	376.0522	1.9
328	377.0519	3.1
329	378.0549	1.2
330	389.0011	6.8
331	390.0362	1.7
332	390.9938	3.1
333	393.0702	4.4
334	394.0509	1.6
335	394.9936	1.0
336	395.0428	1.6
337	399.0558	1.5
339	405.7065	2.2
340	411.0175	1.3
341	425.0632	1.3
342	427.0073	2.2
343	427.0468	2.0
344	427.0825	1.7
345	429.0275	1.5
346	430.9931	1.5

NUMBER 408

6-1/2"
9-1/8"
BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)